Table 1-1 • Quality Assurance Objectives for Measurement Data - KAR Laboratories
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

Fraction	Analyte	Water Matrix		Soil Matrix	
		%Recovery	RPD	%Recovery	RPD
Metals (6020)	Arsenic	73 - 118	18	40 - 129	17
	Barium	69 - 124	10	55 - 132	10
	Cadmium	69 - 120	12	86 - 103	14
	Chromium	68 - 119	24	69 - 118	20
	Copper	63 - 118	10	75 - 125	27
	Lead	68 - 143	10	57 - 131	35
	Selenium	60 - 121	10	49 - 116	25
	Silver	71 - 114	20	82 - 105	28
	Zinc	64 - 123	10	61 - 131	19
Metals (7000 series)	Mercury	78 - 121	12	71 - 128	13
General	Cyanide, Total	84 - 112	10	81 - 111	13
Volatile Organic Compounds	1,2-Dichloroethane-d4 (surrogate)	82 - 126	NA	87 - 126	NA
	Toluene-d8 (surrogate)	87 - 105	NA	87 - 105	NA
	Bromofluorobenzene (surrogate)	95 - 116	NA	95 - 116	NA
	1,1-Dichloroethene	83 - 133	21	83 - 133	21
	Benzene	66 - 147	19	66 - 147	19
	Trichloroethene	74 - 121	18	74 - 121	18
	Toluene	81 - 135	17	81 - 135	17
	Chlorobenzene	85 - 137	19	85 - 137	19
Semivolatile Organic Compounds (base/neutral extractables)	Nitrobenzene-d5 (surrogate)	35 - 144	NA	23 - 120	NA
	2-Fluorobiphenyl (surrogate)	43 - 116	NA	30 - 115	NA
	Terphenyl-d14 (surrogate)	33 - 114	NA	18 - 137	NA
	1,4-Dichlorobenzene	D - 90	22	11 - 108	32
	N-Nitrosodi-n-propylamine	13 - 124	21	1 - 130	26
	1,2,4-Trichlorobenzene	D - 88	28	20 - 101	45
	Acenaphthene	6 - 101	17	28 - 99	27
	2,4-Dinitrotoluene	34 - 123	17	6 - 125	37
	Pyrene	3 - 114	43	D - 137	23
Semivolatile Organic Compounds (acid extractables)	Phenol-d5 (surrogate)	10 - 110	NA	24 - 113	NA
	2-Fluorophenol (surrogate)	21 - 110	NA	25 - 121	NA
	2,4,6-Tribromophenol (surrogate)	10 - 123	NA	19 - 122	NA
	Phenol	D - 90	24	1 - 136	25

Table 1-1 • Quality Assurance Objectives for Measurement Data - KAR Laboratories
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

Fraction	Analyte	Water Matrix		Soil Matrix	
		%Recovery	RPD	%Recovery	RPD
	2-Chlorophenol	D - 101	24	D - 149	29
	4-Chloro-3-methylphenol	33 - 120	18	42 - 129	28
	4-Nitrophenol	D - 127	35	D - 137	36
	Pentachlorophenol	29 - 136	17	D - 137	50
Polychlorinated Biphenyls (PCBs)	TCMX (surrogate)	D - 70	NA	24 - 83	NA
	DCB (surrogate)	28 - 116	NA	30 - 117	NA
	Arochlor-1242	10 - 118	41	33 - 126	35

Table 1-2 • Quality Assurance Objectives for Measurement Data - TriMatrix Laboratories
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

Fraction	Analyte	Water Matrix		Soil Matrix	
		%Recovery	RPD	%Recovery	RPD
Metals (6020)	Arsenic	59 - 164	20	60 - 141	20
	Barium	53 - 142	20	69 - 131	20
	Cadmium	74 - 127	20	65 - 134	20
	Chromium	76 - 127	20	43 - 148	20
	Copper	73 - 122	20	47 - 144	20
	Lead	75 - 134	20	74 - 132	20
	Selenium	59 - 155	20	51 - 137	20
	Silver	69 - 128	20	47 - 132	20
	Zinc	61 - 141	20	78 - 119	20
Metals (7000 series)	Mercury	59 - 158	20	73 - 136	20
General	Cyanide, Total	59 - 151	20	47 - 149	20
Volatile Organic Compounds	1,2-Dichloroethane-d4 (surrogate)	80 - 119	NA	82 - 116	NA
	Toluene-d8 (surrogate)	82 - 117	NA	81 - 117	NA
	Bromofluorobenzene (surrogate)	70 - 120	NA	74 - 126	NA
	Dibromofluoromethane (surrogate)	75 - 124	NA	77 - 124	NA
	1,1-Dichloroethene	50 - 143	28	63 - 134	24
	Benzene	71 - 125	42	74 -130	22
	Trichloroethene	61 - 133	40	70 - 132	23
	Toluene	69 - 130	38	56 - 137	24
	Chlorobenzene	74 - 129	44	55 - 134	22
Semivolatile Organic Compounds (base/neutral extractables)	Nitrobenzene-d5 (surrogate)	30 - 142	NA	25 - 136	NA
	2-Fluorobiphenyl (surrogate)	34 - 122	NA	31 - 121	NA
	o-Terphenyl (surrogate)	42 - 111	NA	33 - 114	NA
	1,4-Dichlorobenzene	43 - 118	21	43 - 122	27
	N-Nitrosodi-n-propylamine	38 - 128	20	48 - 120	23
	1,2,4-Trichlorobenzene	43 - 113	21	57 - 116	24
	Acenaphthene	36 - 117	19	47 - 112	22
	2,4-Dinitrotoluene	45 - 134	47	52 - 128	22
	Pyrene	35 - 129	14	42 - 129	20
Semivolatile Organic Compounds (acid extractables)	Phenol-d6 (surrogate)	4 - 54	NA	28 - 133	NA
	2-Fluorophenol (surrogate)	8 - 91	NA	18 - 133	NA
	2,4,6-Tribromophenol (surrogate)	23 - 152	NA	10 - 138	NA

Table 1-2 • Quality Assurance Objectives for Measurement Data - TriMatrix Laboratories
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

Fraction	Analyte	Water Matrix		Soil Matrix	
		%Recovery	RPD	%Recovery	RPD
	Phenol	3 - 65	43	58 - 126	21
	2-Chlorophenol	39 - 116	23	51 - 126	16
	4-Chloro-3-methylphenol	43 - 117	19	61 - 125	21
	4-Nitrophenol	1 - 69	42	34 - 128	24
	Pentachlorophenol	7 - 147	35	20 - 143	36
Polychlorinated Biphenyls (PCBs)[1]	TCMX (surrogate)	33 - 131	NA	32 - 152	NA
	DCB (surrogate)	5 - 131	NA	25 - 151	NA
	Aroclor-1016	52 - 135	33	70 - 155	20
	Aroclor-1221	46 - 134	45	54 - 157	23
	Aroclor-1232	54 - 129	40	80 - 120	20
	Aroclor-1242	55 - 141	29	55 - 147	17
	Aroclor-1248	39 - 141	27	65 - 151	13
	Aroclor-1254	38 - 148	24	66 - 148	24
	Aroclor-1260	24 - 164	17	44 - 155	20

[1] One of the listed Aroclors will be used for matrix spike determination at TriMatrix.

Table 1-3 • Quality Assurance Objectives for Measurement Data - Field
Quality Assurance Project Plan - City of Kalamazoo Brownfields Projects
January 2001

Parameter	RL	RPD
pH	0.1 s.u.	±0.1 s.u.
Specific Conductance	0.1 μmhos/cm	± 3%
Turbidity	0.5 NTU	±10%
Dissolved Oxygen	0.1 mg/L	±10%
Eh	5 mV	±10 mV

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Table 2-1 • Sample Container, Preservation, and Holding Time Requirements

Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
January 2001

Parameter	Matrix	Container	Chemical Preservative[1]	Maximum Holding Time
Metals	water	500 mL plastic	1:1 nitric acid to pH < 2	180 days[2]
	soil	4 oz. glass jar	None	180 days[2]
Cyanide, Total	water	500 mL plastic	4 - 5 sodium hydroxide pellets to pH > 12	14 days
	soil	2 oz glass jar	None	14 days
Volatile Organic Compounds	water	2 X 40 mL glass vial	1:1 hydrochloric acid to pH < 2[4]	14 days
	soil	2 oz. amber glass	Methanol, 1:1 weight/volume ratio	14 days
Semivolatile Organic Compounds	water	1000 mL amber glass	None	7 days/40 days[3]
	soil	4 oz. glass jar	None	14 days/40 days[3]
Polychlorinated Biphenyls (PCBs)	water	1000 mL amber glass	None	7 days/40 days[3]
	soil	4 oz. glass jar	None	14 days/40 days[3]

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[1] All samples must be iced at the time of collection.
[2] Hold time for mercury is 28 days.
[3] Sample must be extracted within 7 days of collection; extract must be analyzed within 40 days of extraction.
[4] Vials are pre-preserved with 0.5 mL 1:1 hydrochloric acid.

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
6020	Arsenic	20	100	0.113	20	4.542	100	0.281	20	27	100
	Barium	100	1,000	0.374	100	15.0	1,000	0.581	100	56	500
	Cadmium	0.5	50	0.015	0.5	0.608	50	0.017	0.5	15	50
	Chromium, Total	5	500	0.083	5	200	500	0.147	5	61	500
	Copper	5	1,000	0.094	5	75.6	1,000	0.657	5	25	1,000
	Lead	3	1,000	0.060	3	290.4	1,000	0.210	3	105	1,000
	Selenium	5	200	0.486	5	19.43	200	0.288	5	102	200
	Silver	0.2	500	0.064	0.214	140.0	500	0.028	0.2	9	500
	Zinc	20	1,000	0.164	20	92.1	1,000	0.419	20	52	1,000
7470(w)/7471(s)	Mercury	0.2	100	0.074	0.2	6.183	100	0.081	0.2	8	100
9014	Cyanide, Total	5	200	1.16	5	46.3	200	1	5	59	200
8260	Acetone	100	5,000	8.46	100	423	5,000	1.028	100	1.028	5,000
	Acrylonitrile	1	2,500	0.957	1	93.9	2,500	0.108	1	0.108	2,500
	Benzene	1	50	0.081	1	4.05	50	0.100	1	0.100	50
	Bromochloromethane	1	100	0.312	1	15.6	100	0.329	1	0.329	100
	Bromodichloromethane	1	100	0.071	1	3.55	100	0.074	1	0.074	100
	Bromoform	1	100	0.074	1	3.70	100	0.089	1	0.089	100

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	Bromomethane	1	250	0.417	1	20.8	250	0.313	1	0.313	250
	Methyl Ethyl Ketone	50	2,500	4.07	50	203.5	2,500	1.205	50	1.205	2,500
	Carbon Disulfide	5	250	1.181	5	59.05	250	0.134	5	0.134	250
	Carbon Tetrachloride	1	50	0.076	1	3.80	50	0.085	1	0.085	50
	Chlorobenzene	1	50	0.056	1	2.80	50	0.106	1	0.106	50
	Chloroethane	1	250	0.114	1	5.70	250	1.000	1	1.000	250
	Chloroform	1	50	0.056	1	2.80	50	0.076	1	0.076	50
	Chloromethane	1	250	0.148	1	7.40	250	0.118	1	0.118	250
	Dibromochloromethane	1	100	0.097	1	4.85	100	0.076	1	0.076	100
	1,2-Dibromo-3-chloropropane	1	250	0.262	1	13.1	250	0.474	1	0.474	250
	Dibromomethane	5	250	0.096	5	4.80	250	0.067	5	0.067	250
	1,2-Dibromoethane	1	250	0.097	1	4.85	250	0.088	1	0.088	250
	1,2-Dichlorobenzene	1	100	0.049	1	2.45	100	0.168	1	0.168	100
	1,3-Dichlorobenzene	1	100	0.072	1	3.60	100	0.171	1	0.171	100
	1,4-Dichlorobenzene	1	100	0.075	1	3.75	100	0.191	1	0.191	100
	trans-1,4-dichloro-2-butene	–	--	0.901	1	45.05	100	0.670	1	0.670	100
	Dichlorodifluoromethane	1	100	0.070	1	3.50	100	0.092	1	0.092	100
	1,1-Dichloroethane	1	50	0.113	1	5.65	50	0.049	1	0.049	50

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	1,2-Dichloroethane	1	50	0.087	1	4.35	50	0.148	1	0.148	50
	1,1-Dichloroethene	1	50	0.185	1	9.25	50	0.129	1	0.129	50
	cis-1,2-Dichloroethene	1	50	0.122	1	6.20	50	0.097	1	0.097	50
	trans-1,2-Dichloroethene	1	50	0.135	1	6.75	50	0.039	1	0.039	50
	Diethyl ether	50	2,500	0.360	10	18.0	2,500	0.276	50	0.276	2,500
	1,2-Dichloropropane	1	50	0.117	1	5.85	50	0.057	1	0.057	50
	cis-1,3-Dichloropropene	1	50	0.092	1	4.60	50	0.064	1	0.064	50
	trans-1,3-Dichloropropene	1	50	0.049	1	2.45	50	0.094	1	0.094	50
	Ethylbenzene	1	50	0.040	1	2.0	50	0.066	1	0.066	50
	2-Hexanone	50	2,500	1.793	50	89.65	2,500	0.105	50	0.105	2,500
	Isopropylbenzene	1	100	0.054	1	2.7	100	0.049	1	0.049	100
	Methylene Chloride	5	250	0.197	5	9.85	250	0.475	5	0.475	250
	Iodomethane	–	--	0.469	1	23.45	100	0.132	1	0.132	--
	Methyl Isobutyl Ketone	50	2,500	0.960	50	480	2,500	0.697	50	0.697	2,500
	Methyl (tert) Butyl Ether	5	250	0.849	5	42.45	250	0.062	5	0.062	250
	Naphthalene	5	330	0.205	5	10.25	330	0.180	5	0.180	330
	N-Propylbenzene	1	100	0.085	1	4.25	100	0.122	1	0.122	100
	Styrene	1	50	0.103	1	5.15	50	0.062	1	0.062	50

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	1,1,1,2-Tetrachloroethane	1	100	0.147	1	7.35	100	0.132	1	0.132	100
	1,1,2,2-Tetrachloroethane	1	100	0.076	1	3.80	100	0.228	1	0.228	100
	Tetrachloroethene	1	50	0.171	11	8.55	50	0.098	1	0.098	50
	Toluene	1	100	0.109	11	5.45	100	0.106	1	0.106	100
	1,2,4-Trichlorobenzene	5	330	0.060	5	3.0	330	0.128	5	0.128	330
	1,1,1-Trichloroethane	1	50	0.090	1	4.5	50	0.114	1	0.114	50
	1,1,2-Trichloroethane	1	50	0.155	1	7.75	50	0.098	1	0.098	50
	Trichloroethene	1	50	0.107	1	5.35	50	0.094	1	0.094	50
	Trichlorofluoromethane	1	100	0.043	1	2.15	100	0.128	1	0.128	100
	1,2,3-Trichloropropane	1	100	0.123	1	6.15	100	0.255	1	0.255	100
	1,2,4-Trimethylbenzene	1	100	0.060	1	3.00	100	0.128	1	0.128	100
	1,3,5-Trimethylbenzene	1	100	0.059	1	2.95	100	0.103	1	0.103	100
	Vinyl Chloride	1	100	0.116	1	5.80	100	0.122	1	0.122	100
	Xylenes, Total	3	150	0.153	3	7.65	150	0.241	3	0.241	150
8270	Bis(2-Chloroethyl)ether	5	330	1.514	5	265	330	0.176	5	2.2	330
	Bis(2-chloroisopropyl)ether	5	330	1.434	5	68.7	330	0.165	5	1.8	330
	N-Nitrosodi-N-propylamine	5	330	1.561	5	126	330	0.340	5	1.1	330
	Hexachloroethane	5	330	1.431	5	90.6	330	0.154	5	1.2	330

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	Nitrobenzene	5	330	0.919	5	127	330	0.132	5	2.2	330
	Isophorone	5	330	1.530	5	56.4	330	0.185	5	1.4	330
	Bis(2-chloroethoxy)methane	5	330	1.444	5	151	330	0.110	5	1.2	330
	Naphthalene	5	330	1.339	5	136	330	0.141	5	1.5	330
	4-Chloroaniline	20	1,300	0.896	20	144	1,300	0.098	20	0.6	1,300
	Hexachlorobutadiene	5	330	1.260	5	219	330	0.124	5	1.2	330
	2-Methylnaphthalene	5	330	1.567	5	120	330	0.078	5	1.1	330
	Hexachlorocyclopentadiene	5	330	0.608	5	209	330	0.041	5	0.8	330
	2-Nitroaniline	20	1,700	1.063	20	166	1,700	0.107	20	1.2	1,700
	Dimethylphthalate	5	330	1.296	5	120	330	0.076	5	1.3	330
	2,6-Dinitrotoluene	5	330	0.892	5	56.0	330	0.224	5	1.6	330
	Acenaphthylene	5	330	1.290	5	97.8	330	0.090	5	1.4	330
	3-Nitroaniline	20	1,700	1.196	20	66.3	1,700	0.221	20	0.6	1,700
	Acenaphthene	5	330	0.956	5	129	330	0.092	5	1.0	330
	Dibenzofuran	5	330	1.401	5	74.4	330	0.097	5	1.7	330
	2,4-Dinitrotoluene	5	330	0.278	5	68.6	330	0.347	5	1.5	330
	Benzo(b)fluoranthene	5	330	1.388	5	50.1	330	0.137	5	1.8	330
	Diethyl Phthalate	5	330	1.493	5	120	330	0.092	5	1.3	330

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	Fluorene	5	330	0.659	5	105	330	0.128	5	1.2	330
	4-Chlorophenyl Phenyl Ether	5	330	1.373	5	123	330	0.163	5	1.3	330
	4-Nitroaniline	20	1,700	0.852	20	64.2	1,700	0.117	20	0.8	1,700
	N-Nitrosodiphenylamine	5	330	0.905	5	75.6	330	0.063	5	0.4	330
	4-Bromophenyl Phenyl Ether	5	330	1.162	5	73.9	330	0.048	5	1.2	330
	Hexachlorobenzene	5	330	1.163	5	139	330	0.051	5	1.1	330
	Phenanthrene	5	330	1.324	5	34.2	330	0.115	5	1.2	330
	Anthracene	5	330	0.751	5	94.6	330	0.053	5	1.1	330
	Di-n-Butyl Phthalate	5	330	0.817	5	104	330	0.243	5	1.8	330
	Fluoranthene	5	330	0.568	5	120	330	0.076	5	1.1	330
	Pyrene	5	330	0.964	5	152	330	0.158	5	1.5	330
	Butyl Benzyl Phthalate	5	330	1.390	5	130	330	0.220	5	2.0	330
	3,3'-Dichlorobenzidine	20	2,000	0.754	20	64.4	2,000	0.092	20	0.7	2,000
	Bis(2-ethylhexyl)phthalate	5	330	1.044	5	75.3	330	0.104	5	3.0	330
	Benzo(a)Anthracene	5	330	0.899	5	153	330	0.104	5	1.6	330
	Chrysene	5	330	0.747	5	123	330	0.112	5	1.4	330
	Di-n-Octylphthalate	5	330	1.209	5	77.9	330	0.145	5	2.0	330
	Benzo(k)Fluoranthene	5	330	1.423	5	133	330	0.184	5	1.9	330

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
	Benzo(a)pyrene	5	330	0.939	5	67.5	330	0.108	5	1.8	330
	Ideno(1,2,3-cd)Pyrene	5	330	1.258	5	79.9	330	0.078	5	1.0	330
	Dibenzo(a,h)Anthracene	5	330	1.306	5	167	330	0.090	5	1.6	330
	Benzo(g,h,i)Perylene	5	330	1.096	5	64.4	330	0.115	5	1.1	330
	Phenol	5	330	0.743	5	48.5	330	0.129	5	1.1	330
	2-Chlorophenol	5	330	1.426	5	14.4	330	0.101	5	1.0	330
	2-Methylphenol	5	330	1.362	5	120	330	0.128	5	1.1	330
	4-Methylphenol	5	330	1.547	5	85.4	330	0.110	5	0.8	330
	2-Nitrophenol	5	330	0.796	5	167	330	0.255	5	1.9	330
	2,4-Dimethylphenol	5	330	1.538	5	132	330	0.158	5	0.2	330
	2,4-Dichlorophenol	10	330	1.476	10	117	330	0.117	10	0.8	330
	4-Chloro-3-Methylphenol	5	330	1.558	5	97.2	330	0.110	5	1.0	330
	2.4.6-Trichlorophenol	5	330	1.306	5	144	330	0.121	5	1.4	330
	2,4,5-Trichlorophenol	5	330	1.380	5	178	330	0.074	5	1.2	330
	2,4-Dinitrophenol	20	1,700	0.685	20	255	1,700	0.253	20	0.5	1,700
	4-Nitrophenol	20	1,700	1.192	20	390	1,700	0.191	20	1.6	1,700
	4.6-Dinitro-2-methylphenol	20	1,700	1.836	20	462	1,700	0.221	20	0.8	1,700
	Pentachlorophenol	20	1,700	0.733	20	95.2	1,700	0.143	20	2.4	1,700

Table 2-2 • Analytical Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

EPA Method Reference	Parameter	Part 201 TDL		KAR Laboratories				TriMatrix Laboratories			
				water[1]		soil[2]		water[1]		soil[2]	
		water	soil	MDL	RL	MDL	RL	MDL	RL	MDL	RL
8020	Aroclor-1016	0.2	330	0.028	0.2	16.6	330	0.010	0.2	1.0	330
	Aroclor-1260	0.2	330	0.014	0.2	20.8	330	0.014	0.2	1.0	330
	Aroclor-1232	0.4	330	NA	0.4	NA	330	0.070	0.4	11	330
	Aroclor-1242	0.2	330	NA	0.2	NA	330	0.094	0.2	11	330
	Aroclor-1248	0.2	330	NA	0.2	NA	330	0.060	0.2	8.0	330
	Aroclor-1221	0.2	330	NA	0.2	NA	330	0.074	0.2	3.0	330
	Aroclor-1254	0.2	330	NA	0.2	NA	330	0.060	0.2	9.0	330

[1] in μg/L
[2] in μg/Kg
NA = Not available

Table 2-3 • Sample Preparation Methods
Quality Assurance Project Plan - City of Kalamazoo Brownfield Projects
November 2000

Analysis	Water		Soil	
	EPA Method Reference	KAR SOP Number	EPA Method Reference	KAR SOP Number
Digestion - Metals	3010A	KM301.01	3050B	KM3050B.01
Digestion - Mercury	7470	KM7470	7471A	KM7471A
Distillation - Cyanide	9010B	KG251.01	–	NA
Extraction/Prep - VOCs	5030	KO8260HP.01	5035	KO5035H.01
Extraction/Prep - SVOCs	3510C	KO3510.01	3545	KO3545.01
Extraction/Prep - PCBs	3510C	KO3510.01	3545	KO3545.01
Analysis	Water		Soil	
	EPA Method Reference	TriMatrix SOP Number	EPA Method Reference	TriMatrix SOP Number
Digestion - Metals	3010A	GR-01-121	3050B	GR-01-103
Digestion - Mercury	7470	GR-01-123	7471A	GR-01-109
Distillation - Cyanide	9012A	GR-18-109	9010B	GR-18-106
Extraction/Prep - VOCs	5030	GR-04-104	5035	GR-04-105
Extraction/Prep - SVOCs	3510C	GR-09-101	3550	GR-09-103
Extraction/Prep - PCBs	3510C	GR-09-107	3550B	GR-09-108

STANDARD OPERATING PROCEDURE **SOP 14-04**

Field Screening for Volatile Organic Compounds in Soil Using a Photoionization Analyzer

11/20/1996; Revised 11/20/1996

Scope: This SOP describes the technique required for field screening of soil samples for volatile organic compounds (VOCs).This method can be used to select soil samples for laboratory analysis, to aid in the placement of monitor well screens, or to aid in the evaluation of a site for the extent of VOC contamination. This method is intended to provide qualitative data only.

Equipment: HNu Systems PI-101.
Gas bags and valves for calibration gas.

Reagents: Organic free water.
100-ppm isobutylene in air standard.

Procedures:

A. Instrument Calibration

1. Fill a Tedlar® gas bag with the appropriate isobutylene standard gas, close transfer valve, and remove gas cylinder from gas bag.

2. Connect the HNu to the gas bag and open the transfer valve.

3. Adjust gas select until the display reads 68 ppm (including appropriate multiplier).

4. Ensure the lamp is lit when reading standard.

5. The HNu should be calibrated every 4 hours using a 100-ppm isobutylene in air standard. If elevated concentrations are anticipated, calibration should be performed using a 1000-ppm methane standard as well.

B. Sample Measurement

1. Place the probe inlet at the surface of the sample or area to be measured. Move the probe along the surface while observing the instrument readout.

2. If an increased meter reading is observed, slowly sample the area where the reading is indicated until the maximum reading is obtained. Record in field notebook.

Scope: This SOP describes the use of a handheld flame ionization detector (FID) to measure the concentration of volatile organic compounds (VOCs) in soil or groundwater samples. This technique provides qualitative data only and is typically used as a screening method to determine which samples should be analyzed by a higher data quality method.

Discussion: This method provides an indirect indication of soil contaminant concentration by measuring the organic constituents that partition into the headspace. FIDs use a hydrogen flame to ionize organic vapors. The measured electrical current that is generated by the free ions, called the instrument response, is related to the concentration of volatile compounds present in the sample. While FIDs provide signficant response to most organic vapors, they are more sensitive to aliphatic (chained) hydrocarbons because these compounds burn more efficiently than aromatic (ringed) hydrocarbons.

Equipment: Photovac MicroFID I/S Flame Ionization Detector
MicroFID refill adapter, Photovac Part No. 396004
Calibration kit, Photovac Part No. 396011
Charcoal filter, Photovac Part No. 396021
Battery pack, Photovac Part No. 396005
Inlet filter, Photovac Part No. 396020

Reagents: Hydrogen gas, 99.999%, Grade 5
Calibration gas, 100 ppm methane in air, Photovac Part No. 396028

Procedure:

A. Warnings and Safety Practices

1. Compressed gases

a. Compressed gas cylinders must be handled with extreme care. Secure the hydrogen and calibration gas cylinders before use. Store in an upright position away from ignition sources.

b. Do not expose the cylinders to direct sunlight or heat the cylinders. Cylinders may rupture at high temperatures.

c. Use only the specified regulator for the calibration gas. Use only the MicroFID refill adaptor for the hydrogen gas.

d. Do not drag or roll cylinders. Use a hand truck to move large cylinders.

e. Safety glasses should be worn when working with compressed gases.

2. Compressed gas regulators

   a. Do not use the regulator as a shut-off valve. Close the cylinder when not in use.

   b. Do not subject the regulator to an inlet pressure greater than recommended.

   c. Do not detach the regulator when it is under pressure or it is in use.

   d. Turn the pressure control valve on the cylinder all the way out (close the cylinder). Turn the regulator outlet to off. Open the gas cylinder valve slowly and check for leaks. Adjust the delivery pressure and then open the regulator valve.

3. Hydrogen gas

   Hydrogen gas is a fire and explosion hazard when exposed to heat or a source of ignition. The lower explosive limit (LEL) is 4%. The LEL is the minimum concentration of a gas or vapor in air that will ignite in the presence of a source of heat or sparks. Refer to the MSDS before handling this gas.

4. Calibration gas

   Adequate ventilation should be provided when calibrating the MicroFID.

5. Battery Packs

   a. Do not leave the battery packs uncharged for an extended period of time as this will result in damage to the packs and possible loss of logged data.

   b. Leaving the MicroFID for more than 3 months without powering it on may result in loss of recorded data and setup parameters. If not used for long periods of time, the instrument should be powered on for a few hours each month to avoid loss of data.

   c. The battery pack is 57% lead by weight. Do not open the battery pack. Dispose of properly or return to Photovac for recycling.

B. Operation

1. Power the instrument on by pressing the front of the ON/OFF switch. Once powered, the version number and creation date of the software will be displayed. Press ENTER.

2. To start the flame, use the arrow keys to select "start flame" and press ENTER.

3. At the prompt, start the flow of hydrogen by turning the shut-off valve counterclockwise to start the hydrogen gas flow and press ENTER. The pump will start and the MicroFID will ignite the flame. There will be a small "pop" when the flame has been ignited.

4. Once the flame has been started, the default display will be shown. The instrument status will appear at the left of the upper line of the display. If more than one status is in effect, the status with the highest priority will be displayed until the condition is corrected or the option is turned off. Refer to the user's manual, Section 2.1, for status code information.

5. Press BATT key to check battery voltage. When the voltage drops below 7.2 volts, a "LoBatt" status will be displayed and the battery pack must be recharged. A fully charged battery powers the MicroFID for approximately 15 hours.

C. Calibration

When calibrating the MicroFID, be sure that the instrument is level. If the instrument is tilted side to side, gravity will affect the flame height and cause erroneous readings.

1. Prepare the calibration gas bag following the procedure outlined in the user's manual, Section 3, pages 34 - 36.

2. Press CAL and select the desired CAL memory. (Cal memories store the response factor, zero point, sensitivity, and alarm level. Cal memories are established using the procedure described in the user's manual, Section 3.1.4, pages 37 - 38). Enter the desired response factor and press ENTER. Refer to Appendix 8.6 in the user's manual for a list of response factors. If the compound of interest is not listed in Appendix 8.6 or if mixture of gases will be measured, enter a response value of 1.

3. Select LOW range or HIGH range and press ENTER. Low range should be used for an anticipated concentration range of 0.5 - 2000 ppm (methane equivalents). Use high range for an expected concentration range of 10 - 50,000 ppm (methane equivalents)

4. To set the zero point using room air, press ENTER. If using a charcoal filter, connect the filter as follows:

   a. Load the teflon ferrules into the nut and connect the nut to the MicroFID inlet. DO NOT TIGHTEN.

   b. Remove the charcoal filter from the plastic bag and insert into the nut. Finger tighten. If the filter is not secure, ensure that the tube stub is inserted far enough into the nut. Do not over tighten the fitting.

   c. Press ENTER to set the zero point.

A charcoal filter should be used if the quality of the ambient air is unknown. The charcoal filter will remove hydrocarbon contaminants for up to 4000 ppm hours. In other words, the filter will be good for 1 hour removing 4000 ppm of hydrocarbon contaminants or 4 hours removing 1000 ppm. An increases hydrocarbon background will be observed when the filter needs replacement.

5. At the prompt, enter the know span gas concentration and connect the gas bag adapter to the inlet. Open the bag and press ENTER. Readings may fluctuate slightly as the gas bag empties. Do not allow the MicroFID to evacuate the bag completely.

6. When the display reverts to normal, the unit is calibrated and ready for use. Remove the span gas bag from the inlet.

7. Press the ALARM key and enter the alarm level for the selected CAL memory.

8. Sample the bag of calibration gas to ensure proper calibration.

D. Sample Measurement

1. Place the probe inlet at the surface of the sample or area to be measured. Move the probe along the surface while observing the instrument readout.

2. If an increased meter reading is observed, slowly sample the area where the reading is indicated until the maximum reading is obtained. Record in field notebook.

E. Maintenance

1. Battery charging - Refer to user's manual, Section 1.5.

2. Hydrogen cylinder

   a. To empty the hydrogen cylinder, turn the MicroFID off and open the hydrogen shut-off valve.

   b. Remove the battery pack as described in Section 1.5 of the user's manual.

   c. Locate the purge outlet on the underside of the instrument and use the MicroFID multi-tool to turn the screw counterclockwise. Loosen the screw but do not remove it.

   d. Leave the instrument with the purge outlet facing up. This will prevent the hydrogen from venting into the case. A full cylinder will take approximately 15 minutes to empty.

e. When the cylinder is empty (as indicated on the contents gauge), close the purge outlet by turning the screw clockwise.

f. Replace the battery pack.

3. Sample Inlet Filter

a. Replace on a weekly basis or more frequently if the instrument is used in a dusty or wet environment. As the filter collects dust, the inlet flow rate and sensitivity will decrease. Do not replace in a hazardous environment.

b. Turn the instrument off and unscrew the filter housing from the detector housing. Be careful not to lose the O-ring seal.

c. Remove the filter and install a new one with the teflon side facing down in the filter housing and the mesh side facing the instrument. Handle the filter disk by the edges or with forceps as the mesh may be damaged or contaminated by excessive handling. Be sure to remove the blue plastic from the filter prior to installation.

d. Calibrate all Cal Memories before continuing operation. Never operate the MicroFID without an inlet filter.

F. Troubleshooting

Refer to Section 6.0 of the user's manual.

Scope: Procedures outlined in the SOP are intended to provide general instruction for groundwater sampling activities. Field personnel should consult the project work plan for additional information.

Reference: Minnesota Pollution Control Agency, *Groundwater Sampling Guidance: Development of Sampling Plans, Protocols and Reports*, January 1995.

New Jersey Department of Environmental Protection and Energy, *Field Sampling Procedures Manual*, May 1992.

U.S. Environmental Protection Agency-Region IV, *U.S. EPA Environmental Compliance Branch Standard Operating Procedures and Quality Assurance Manual*, February 1, 1991.

Selection of Sampling Equipment:

Factors to consider in selection of appropriate sampling equipment for a project should be based on technical performance of the equipment. A listing of several sampling devices, in order of preference, and their expected degree of sampling alteration are contained in the following table:

Device	Purging	Sampling	Comments
Bladder Pump	Minimal to Slight	Minimal to Slight	Practice required to produce continuous, low flow rate
Low Flow-Rate, Centrifugal, Electric Submersible Pump	Minimal to Slight	Minimal to Slight	Grundfos Redi-Flo2 with low flow-rate controller
Low Flow-Rate, Helical Rotor, Electrical Submersible Pump	Minimal to Slight	Minimal to Slight	Keck Pump with Viton stator and low flow-rate controller
Peristaltic Suction Lift Pump	Slight to Moderate	Moderate to High	May be unsuitable for volatile organics
Bailer	High to Very High	Moderate to High	Can cause substantial alteration of water chemistry. Is highly dependent on sampler's ability to minimize turbulence and aeration of sample.

Procedure:

1. Determine the order in which the wells should be sampled. Typically, sampling order should proceed from the cleanest well to the most contaminated. When no historical water quality data are available, sample background wells first followed by the farthest downgradient wells. The

wells expected to most significantly contaminated should be sampled last. Sampling order is not as critical when a peristaltic pump is used, as the pump tubing is replaced after each use.

2. Obtain the following information prior to the sampling event:

   a. Well depth.
   If not previously measured, determine by subtracting the distance between ground surface and top-of-casing (stick-up) and add this distance to the installation screen depth.

   b. Screen length.

   c. Depth to bottom of screen and depth to top of screen from top-of-casing. Using this information, determine the depth to the midpoint of the well screen.

3. Record the condition of the well in the field notes. Additional information may be required for documentation before, during, and after groundwater sampling. Refer to the project work plan and SOP 10-3 for additional information.

4. Determine static water level using SOP 18-4. Record in the field notebook. Minimize disturbances of the stagnant water column during water level measurement.

   Water levels are measured prior to and possibly during a groundwater sampling event for the following reasons:

   - To assess whether the static water column length is sufficient to allow purging and sampling to proceed in the normal manner provided that drawdown is moderate.
   - To select the depth to which the pump intake, bailer, or other purging or sampling device should be lowered.
   - To monitor the water level during purging and sampling.
   - To determine groundwater flow directions.

   Unless stated in the work plan, groundwater from monitoring wells containing free-product will not be sampled. If the groundwater must be sampled, utilize disposable equipment.

5. Rinse reusable sampling equipment with deionized water before inserting the equipment into the monitoring well.

6. Calibrate field measurement equipment as required by the project work plan.

7. Determine the volume of water to be purged prior to sample collection. The U.S. EPA guidelines recommend that a minimum of three well volumes be purged before a representative sample can be collected.

Calculate the volume of water constituting three well volumes first calculating the linear feet of water in the well (total depth of the well, ft. - depth to water, ft.). Then calculate the amount of water within the well casing by multiplying the linear feet of water by the volume per foot for the proper diameter casing. The capacity of common casing diameters are as follows:

Casing diameter	Gallons/linear foot
2 inch	0.1632
4 inch	0.6528
6 inch	1.4688
8 inch	2.6112
10 inch	4.0800
12 inch	5.8752

Example:

Total depth of well casing	100 ft
Depth to water	-20 ft
Linear feet of water	80 ft
2 inch casing	x 0.1632
amount of water in casing (gallons)	13.06

Multiply the volume of water in the casing by three (3) to determine the minimum volume to be purged from the well prior to sample collection. Record data in the field notes.

7. Rinse the sampling equipment with deionized water prior to inserting the equipment into the well.

8. Insert the sampling equipment into the well and begin extracting groundwater. When using a sampling pump, the pump should be lowered into the well and set just below the water surface.

During purging, lowering of the water level causes cascading of water into the well if the purge rate is greater than the recovery rate of the well. Keep cascading to a minimum by not drawing the water level in the well below the top of the screen. If the water level is already at the top of or within the well screen, select a purging rate that results in minimum drawdown while allowing the well to be purged in a reasonable length of time.

If the pump begins to pump dry, lower it further into the well. Allow the well to recover to provide sufficient water to completely fill the appropriate sample containers, and collect the sample.

10. Record purging start time in the field notes. A calibrated 5-gallon bucket should be used to monitor the volume of water purged. Dipose of all purge water in accordance with the project work plan.

11. Obtain the necessary field parameter measurements after 1 well volume, 2 well volumes, and 3 well volumes have been purged.

12. Fill required sample containers in accordance with the procedures described in SOP 10-10. Record the type of bottle filled, preservatives added, and the time and date of collection in the field notebook. Samples should be collected in the following order:

    a. Field Parameters
    b. Volatile Organics
    c. Semi-Volatile Organics (includes samples for pesticides, herbicides, and PCBs)
    d. General chemistry parameters
    e. Metals

    Refer to project work plan for sample requirements.

13. Decontaminate the equipment after each use in accordance with procedures described in the equipment-specific SOPs.

Scope: This SOP provides guidance for documentation of field activities.

Equipment: Project Field Notebook
Calculator
Pen with waterproof, non-erasable ink
Watch (for time of day)

Procedure:

1. A field notebook must be prepared for each project. The notebook provides for documentation of all field activities, including sample collection and handling, and visual observations.

2. All records must be legible and should be made in waterproof, non-erasable ink. All entries should contain accurate and inclusive documentation of the project activities.

3. If errors are made, corrections must be made by crossing a single line through the error and entering the correct information. All corrections should be initialed and dated. If possible, the correction should be made by the individual making the error.

4. All entries should be dated and the time of the entry recorded. At the end of each day's activity (or entry of a particular event, if appropriate), a diagonal line should be drawn at the conclusion of the entry and initialed indicating the conclusion of the entry or activity. The daily field notes section of the notebook should be completed in chronological order. No blank pages should be found within this section.

5. Field notebook records should include the following information where applicable:

   - Sample collection equipment used
   - Field analytical equipment used
   - Equipment used for physical measurements
   - Calculations, calibration data, and results for field sampling, analytical, and physical measurement equipment
   - Type and number of samples collected along with sample location and identification number
   - Sample handling, packaging, labeling ,and shipping information, including destination.

6. The field notebook should be kept in a secure place during the field activities (e.g., in hand, in sight, locked in field vehicle). Upon completion of the activity, the field notebook should be checked for completeness, and signed and dated. The field notebook will become part of the project file.

Scope: This SOP describes the procedures and documentation required to trace possession and handling of samples from time of collection through receipt by the laboratory.

Equipment: Sample Tags
Custody Seals
Chain-of-Custody (COC) Record
Pen with waterproof, nonerasable ink

Definition:

A samples is considered to be in custody if:

1. It is in one's actual possession,
2. It is in one's view after being in one's possession,
3. It was in one's possession and then secured to prevent tampering, or
4. It is placed in a designated secure area.

Procedure:

1. The field team leader or designate is responsible for proper handling and custody of field samples until they are formally transferred to another person or facility. As few people as possible should handle the samples during the field event.

2. Sample tags (Figure 1) must be completed in waterproof, nonerasable ink and securely affixed to sample containers at the time of collection. All samples must be documented in the field notebook.

3. Samples should be securely wrapped in bubble packing or other suitable packaging material and placed in an insulated shipping container. Samples should be packed in such a way as to minimize the chance for breakage. Bagged ice should be placed on top of the samples to maintain a temperature of 2 - 6°C during transport.

4. Following sample collection, a chain-of-custody record (Figure 2) must be completed. The COC record must accompany the samples to the laboratory. If more than one sample shipping container is used, a separate chain-of-custody form should be completed for each container.

5. The COC must be completed in waterproof, nonerasable ink. If errors are made, corrections should be made by crossing a single line through the error and entering the correct information. All corrections should be initialed and dated.

6. The chain-of-custody record should include the following information:

    - Project name, number, and location
    - Sampler(s) name(s)
    - Name of project manager along with phone and fax number

- Sample date, time, identification and matrix type
- Total number of containers for each sample and type of preservative added

7. Transfer of the samples listed on the COC form must be documented in the spaces provided at the bottom of the form. One of the samplers listed under the sampler(s) section or a designated field sample custodian who receives secured samples from the sampling team and maintains the samples under secure conditions must be the person that originally relinquishes the samples . Both the person relinquishing the samples and the person receiving them must sign the form. Typically the last person receiving the samples should be the laboratory sample custodian.

8. The COC form is a multipage form. The 3 copies should be distributed as follows:

Pink Copy — Removed by FTC&H sampling personnel once sample transfer has been documented. Retained in the project file.

Yellow Copy — Retained by analytical laboratory.

White Copy — Accompanies final data package from laboratory. Retained with data in project file.

9. The completed COC record should be placed in a zip-lock plastic bag and placed inside the sample-shipment container.

10. Custody seals (Figure 3) should be used to seal sample shipping containers which are ready to be transported by means other than the FTC&H sampling team. Custody seals must be completed in waterproof, nonerasable ink and should include the following information:

- Project name.
- Project number.
- Date sealed.
- Signature of person relinquishing the samples.

Custody seals should be placed on the shipping container so that it cannot be opened without breaking the seals.

11. Samples should be delivered to the laboratory as soon as possible after collection. There are basically 3 routes by which samples are transported to the laboratory:

a. Hand delivered by a member of the FTC&H sampling team.

b. Samples are placed in the secured sample area at the FTC&H offices and the field sample custodian arranges for delivery to the laboratory.

c. Samples are shipped via common carrier (e.g., UPS, Federal Express, City Transfer) to the laboratory. In this case, the method of shipment and associated Bill of Lading number must be recorded in the appropriate block on the COC form.

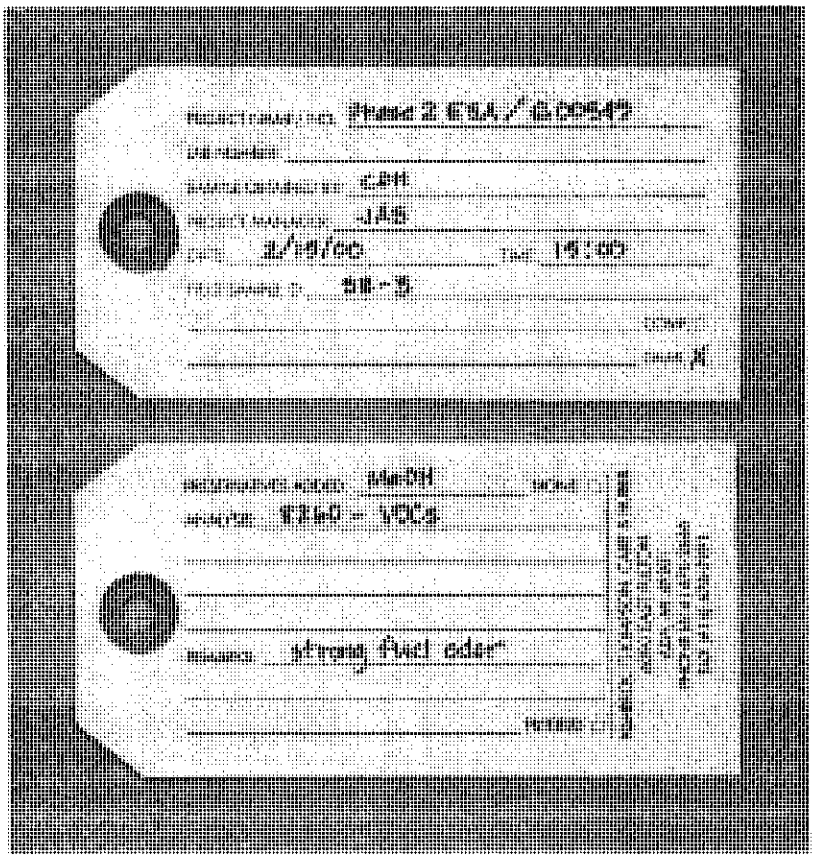
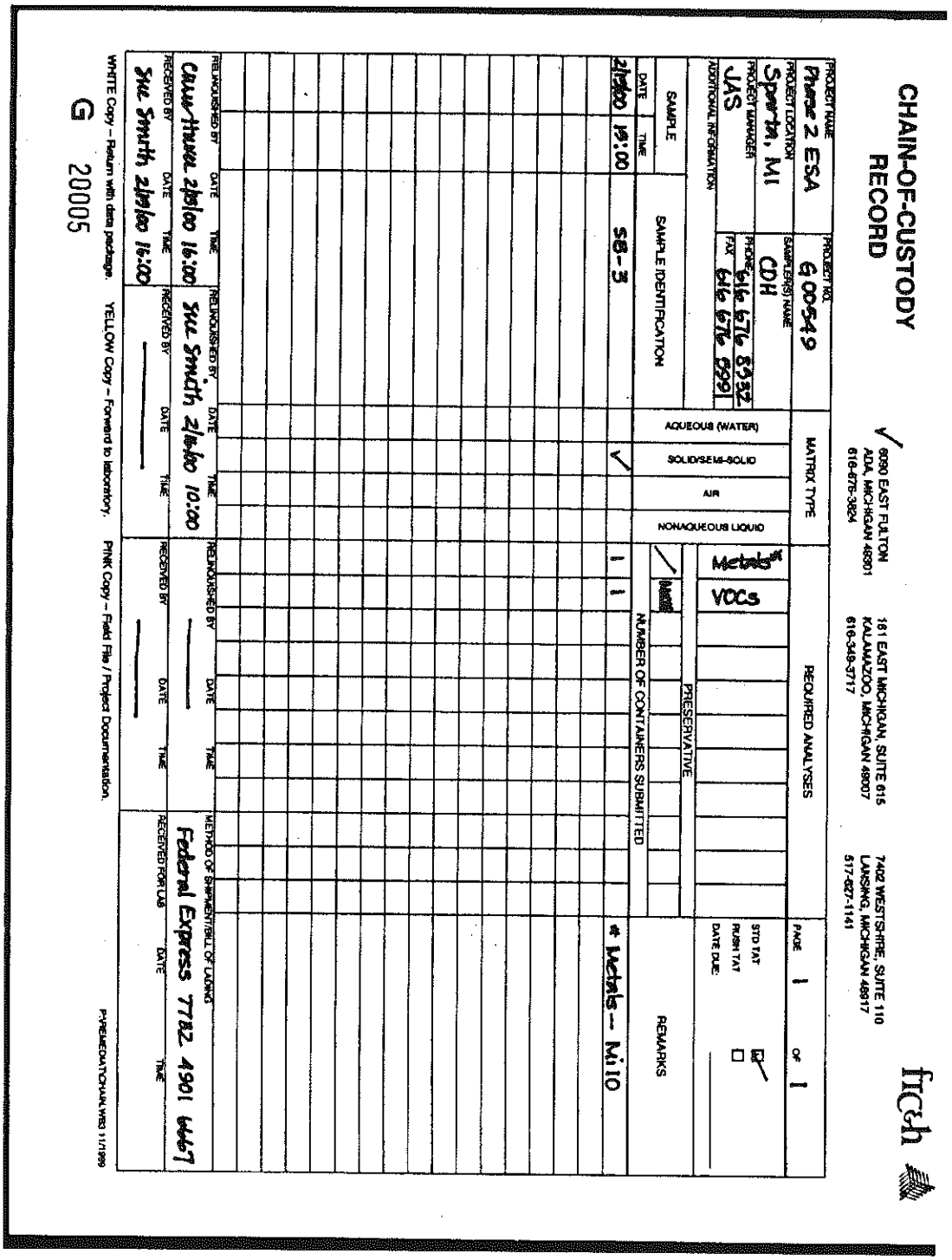


FIGURE 1



CHAIN-OF-CUSTODY RECORD

✓ 8080 EAST FULTON, ADA, MICHIGAN 49301, 616-676-3824
181 EAST MICHIGAN, SUITE 615, KALAMAZOO, MICHIGAN 49007, 616-349-3717
7402 WESTSHIRE, SUITE 110, LANSING, MICHIGAN 48917, 517-627-1141

frc&h

PROJECT NAME: Phase 2 ESA
PROJECT NO.: G 005549
PROJECT LOCATION: Sparta, MI
SAMPLER(S) NAME: CDH
PROJECT MANAGER: JAS
PHONE: 616 676 8332
FAX: 616 676 8399
ADDITIONAL INFORMATION:

MATRIX TYPE: AQUEOUS (WATER); SOLID/SEMI-SOLID; AIR; NONAQUEOUS LIQUID

REQUIRED ANALYSES: Metals; VOCs

PRESERVATIVE

PAGE 1 of 1

STD TAT ☑ RUSH TAT ☐ DATE DUE: _____

SAMPLE DATE	SAMPLE TIME	SAMPLE IDENTIFICATION	MATRIX	NUMBER OF CONTAINERS SUBMITTED	REMARKS
2/9/00	13:00	SB-3	✓	1 1	# Metals -- Mi 10

RELINQUISHED BY: Chad Hawes 2/9/00 16:00 DATE TIME
RECEIVED BY: Sue Smith 2/9/00 16:00 DATE TIME
RELINQUISHED BY: Sue Smith 2/9/00 10:00 DATE TIME
RECEIVED BY: _____ DATE TIME
RELINQUISHED BY: _____ DATE TIME
RECEIVED FOR LAB: _____ DATE TIME

METHOD OF SHIPMENT/BILL OF LADING: Federal Express 7782 4901 4467

WHITE Copy – Return with data package. YELLOW Copy – Forward to laboratory. PINK Copy – Field File / Project Documentation.

G 20005

P:\FIELDDATA\CHAIN.WPD 11/1999

FIGURE 2

frc&h Project Name/No. _____

Signature _____ Date _____

FIGURE 3

frc&h **STANDARD OPERATING PROCEDURE** **SOP 4-06**
Soil Sampling by Hand-Auger Method
07/24/1996; Revised 05/08/00

Scope: This SOP outlines general procedure to be used to acquire soil samples from the surface to a depth of no more than ten feet using a hand auger. This SOP is intended to provide general instruction. Consult the project work plan for additional information.

Reference: ASTM Standard Method 1452-80.

Equipment: Hand auger
Auger extension rods
"T" Handle
Organic vapor measurement instrument

Procedure:

1. Clear the area to be sampled of any surface debris (twigs, rocks, litter). It is advisable to remove the first 3 to 6 inches of surface soil for an area approximately 6 inches in radius around the sampling location.

2. Attach the auger bit to an auger extension rod, and attach the "T" handle to the auger extension rod.

3. Begin augering, periodically removing accumulated soil from around the borehole. This prevents loose material from falling back down the borehole when the auger or extension rods are removed.

4. When the auger has reached desired depth, remove the auger and any loose soil in the borehole. Return auger to bottom of borehole, turn auger and collect sample. Retrieve auger and soil sample.

5. Decontaminate all equipment after use and between sample locations with a soap and water wash followed by a deionized water rinse. Dry equipment with clean paper towel or allow to air dry before further use.

Scope: This SOP describes soil sample collection using a split-barrel sampler with a hollow-stem auger or mud-rotary drilling rig. Procedures outlined in this SOP are meant to provide general instruction for soil sampling activities. Field personnel should consult the project work plan for additional information.

Discussion: Representative samples are collected from discrete intervals using a hardened steel split-barrel sampler. The sampling barrel is advanced by driving with a hammer. Liners or sample retainer baskets may be used. A standard-size sampler will provide sample volume of approximately 400 mL to 700 mL. The sample obtained by this method should not be used for estimation of undisturbed geotechnical or hydrogeological properties.

Reference: ASTM Standard Method D 1586-84.

Equipment:
Hollow-stem auger or mud-rotary drilling rig
Split-barrel sampler
Sampler tube liners
Sample retaining basket
Deionized water
Liquinox® soap solution

Procedure:

1. Soil borings should be advanced incrementally to permit intermittent or continuous sampling. Typically, samples are collected at 5-foot intervals in homogeneous sediment or at changes in lithology between sedimentary layers. Refer to the project work plan for specific information.

2. Once the boring has been advanced to the desired sampling depth, attach the split-barrel sampler to the sampler rods and lower into the borehole. Do not allow the sampler to drop onto the soil to be sampled.

3. Position hammer above and attach the anvil to the top of the sampling rods. Rest the dead weight of the sampler, rods, anvil, and drive weight on the bottom of the borehole and apply a seating blow. Remove sampler assembly if excessive cuttings are encountered and remove cuttings before sample collection.

4. Mark the drill rods in three successive 6-inch increments so that the advance of the sampler can be measured as the hammer is dropped on the sampler assembly. Record the number of blows per 6-inch interval in the field notes.

5. After the sampler has advanced to the necessary depth, retrieve the sampler barrel and open.

6. Record the percent recovery or the length of the sample recovered. Enter soil sample description in field notebook.

7. Measure and record organic vapor content of soil sample and borehole, if required.

8. Soil samples should be collected in accordance with procedures outlined in SOP 4-12.

9. Decontaminate all equipment after use and between sample locations as follows:

   a. Rinse equipment with deionized water.

   b. Wash equipment with soap solution, using a soft-bristled brush made of inert material to remove any particles or surface film.

   c. Rinse thoroughly with deionized water and air dry.

Scope: This SOP outlines basic soil sample handling and preparation procedures. Procedures outlined in this SOP are meant to provide general instruction for soil sampling activities. Field personnel should consult the project work plan for additional information.

References: Boulding, J.R., 1994, *Description and Sampling of Contaminated Soils - A Field Guide*, Second Edition, Lewis Publishers, Ann Arbor.

ASTM Standard Method D 4220-89.

Equipment: Stainless steel spoon, spatula, or wooden tongue depressor
1 - large Pyrex ® glass pan
0-mesh (No. 10, 2 mm) stainless steel screen
Pre-cleaned, pre-preserved sample containers, plastic and glass
Deionized water
Liquinox® soap solution

Procedure:

A. Samples for volatile organic analysis using the EnCore™ sampler

Refer to SOP 14-11, VOCs in Soil - Sample Collection Using EnCore™ Sampler.

B. Samples for volatile organic analysis using the methanol preservation technique

Refer to SOP 14-10, VOCs in Soil - Methanol Preservation Method

C. Samples for semivolatile organics, pesticide, herbicide, or PCB analysis

1. Samples for semivolatile organics, pesticides, herbicides, or PCB analysis should be placed in glass containers with Teflon-lined lids. Sufficient volume should be collected to fill required sample containers. A 2 oz. or 4 oz. jar is typically provided by the laboratory for these tests. No plastic equipment should be used.

2. Prior to sample collection, screen the sample for volatile organics using an OVA, if required. Record instrument readings in field notebook.

3. Review the project work plan to determine whether composite or discrete grab samples should be collected. Samples containing gravel or other large debris should be screened through a precleaned 0-mesh stainless steel screen.

4. Mix the sample in glass pan using a stainless steel spoon, spatula, or wooden tongue depressor.

5. After thorough mixing, spread the soil out evenly in the mixing pan using the mixing tool. Divide the sample into quarters, taking samples from each quarter in a

consecutive manner until the appropriate sample container is filled. Typically, separate sample jars are required for each fraction.

6. Wipe bottle threads to remove any residue and secure cap tightly.

7. Label each sample container and record appropriate information in the field notebook and on the chain-of-custody form.

8. Place samples in an insulated shipping container on ice to maintain sample temperature at 2 - 6°C.

9. Decontaminate all equipment after use and between sample locations as follows:

   a. Rinse well with deionized water.

   b. Wash with soap solution, using a soft-bristled brush made of inert material to remove any particles or surface film.

   c. Rinse thoroughly with deionized water and air dry.

D. Samples for metals or other general analyses

1. Wide mouth plastic bottles may be used for sample collection, with the exception of samples for oil & grease or TPH analysis which should be collected in glass. Sufficient volume should be collected to fill required sample containers. A 250 mL bottle or 4 oz. glass jar is typically provided by the laboratory for these tests.

2. Review the project work plan to determine whether composite or discrete grab samples should be collected. Samples containing gravel or other large debris should be screened through a precleaned 0-mesh stainless steel screen.

3. Mix the sample in glass pan using a stainless steel spoon, spatula, or wooden tongue depressor.

4. After thorough mixing, spread the soil out evenly in the mixing pan using the mixing tool. Divide the sample into quarters, taking samples from each quarter in a consecutive manner until the appropriate sample container is filled.

5. Wipe bottle threads to remove any residue and secure cap tightly.

6. Label each sample container and record appropriate information in the field notebook and on the chain-of-custody form.

7. Place samples in an insulated shipping container on ice to maintain sample temperature at 2 - 6°C.

9. Decontaminate all equipment after use and between sample locations as follows:

   a. Rinse well with deionized water.

   b. Wash with soap solution, using a soft-bristled brush made of inert material to remove any particles or surface film.

   c. Rinse thoroughly with deionized water and air dry.

C. Field Duplicates

Field duplicates are collected as a check of sampling and analytical reproducibility.

1. Sample duplicates should be collected using the same procedure as for the investigative samples. Sample duplicates will be analyzed for the same parameters as the investigative samples and therefore an identical "set" of bottles must be filled.

2. Field duplicates are typically collected at a rate of one for every 10 investigative samples.

D. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD samples are used to evaluate laboratory precision and accuracy. MS/MSD samples are typically analyzed by laboratory as part of their QA/QC program. To insure that project specific matrix spike analysis is performed, it must be requested from the analytical laboratory. Consult the project work plan for sample volume requirements.

Scope: This SOP outlines procedures for groundwater sample handling and preservation. Procedures outlined in this SOP are intended to provide general instruction for groundwater sampling activities. Refer to the project work plan for additional information.

Reference: Minnesota Pollution Control Agency, *Groundwater Sampling Guidance: Development of Sampling Plans, Protocols and Reports*, January 1995.

U.S. Environmental Protection Agency-Region IV, *U.S. EPA Environmental Compliance Branch Standard Operating Procedures and Quality Assurance Manual*, February 1, 1991.

Procedure:

1. An appropriate volume of groundwater must be removed from the monitoring well prior to sample collection. Refer to SOP 10-1 for a general overview of groundwater sampling using the conventional (3 - 5 well volumes) purge method, SOP 10-2 for a general overview of low-flow purge method.

2. Field parameters (pH, specific conductance, Eh, dissolved oxygen, turbidity, and temperature) should be measured using a flow through cell when possible. When ambient measurements are required, use a groundwater containment vessel of sufficient size to allow for temperature equilibration with the atmosphere but with a relatively small surface area exposed to the atmosphere. Measurements should be taken as soon as practical after the groundwater has been removed from the well.

3. After field parameters have been measured, groundwater samples may be collected. Samples should be collected in the following order:

    a. Volatile organics

        1. Three 40 mL vials with Teflon septa should be filled with the groundwater to be tested. Vials are pre-preserved with 1:1 hydrochloric acid solution. Hydrochloric acid is corrosive; gloves should be worn. If the sample preservative comes in contact with the skin, flush with water. Seek medical attention if necessary.

        2. Tilt the vial slightly and with minimum turbulence, fill the vial until it just overflows.

        3. Carefully set the cap in place and screw on firmly.

        4. Invert the vial to check for air bubbles. If air bubbles are present, remove the cap and refill until a sample is obtained with no trapped air.

        5. Label each vial and place samples on ice in an insulated container to maintain sample temperature at 2 - 6°C.

b. Semi-volatile organics (includes samples for acid/base-neutral extractables, pesticides, herbicides, and PCBs)

1. A minimum of 1-amber glass liter bottle is required per scan. No chemical preservation is required.

2. Fill bottle with the groundwater to be tested, allowing minimal headspace for expansion.

3. Label each bottle and place samples on ice in an insulated container to maintain sample temperature at 2 - 6°.

c. General chemistry parameters

1. Container size and type and chemical preservative are dependent on the analyses to be performed. Table 1 provides general information for routinely performed analyses. Refer to the project work plan for specific requirements. The laboratory will provide the required containers and preservatives for the project. Some preservatives are corrosive; gloves should be worn. If the sample preservative comes in contact with the skin, flush with water. Seek medical attention if necessary.

2. Fill each bottle to the shoulder with the groundwater to be tested and cap tightly.

3. Label each bottle and place samples on ice in an insulated container to maintain sample temperature at 2 - 6°.

d. Metals

1. Typically, a 500 mL plastic bottle pre-preserved with 1:1 nitric acid will be supplied by the laboratory for metals. Nitric acid is corrosive; gloves should be worn. If the sample preservative comes in contact with the skin, flush with water. Seek medical attention if necessary.

2. Samples for dissolved metals must be field-filtered prior to preservation.

   a. Attach a 0.45 μm in-line filter cartridge unit onto the discharge line from the sampling device and adjust the discharge and flow rate with a three-way valve system, if necessary. A new cartridge must be used at each sampling location.
   b. Discharge the required volume of filtered groundwater to waste as specified by the filter manufacturer.
   c. Fill the required sample container to the bottle shoulder with the filtered groundwater and cap tightly.
   d. Label the bottle and place sample on ice in an insulated container to maintain sample temperature at 2 - 6°.

3. When total metals are required, fill the sample container provided to the bottle shoulder with the groundwater to be tested and cap tightly.

4. Label the bottle and place sample on ice in an insulated container to maintain sample temperature at 2 - 6°.

Table 1 • Sample Container Type, Size, and Preservative - Routine Groundwater Analyses

Analysis	Container Type	Required Volume	ChemicalPreservative
Alkalinity (all forms)	Plastic	100 mL	None
BOD	Plastic	500 mL	None
Chloride	Plastic	100 mL	None
COD	Plastic	50 mL	1:1 sulfuric acid
Chromium, Hexavalent	Plastic	100 mL	None
Cyanide	Plastic	250 mL	Sodium Hydroxide
Fluoride	Plastic	100 mL	None
N, Ammonia	Plastic	250 mL	1:1 sulfuric acid
N, Total Kjeldahl	Plastic	250 mL	1:1 sulfuric acid
N, Nitrate	Plastic	100 mL	None
N, Nitrite	Plastic	100 mL	None
Phenols, Recoverable	Glass	500 mL	1:1 sulfuric acid
Phosphorus	Plastic	100 mL	1:1 sulfuric acid
Solids (all types)	Plastic	250 mL	None
Sulfate	Plastic	250 mL	None
TOC	Plastic	250 mL	1:1 sulfuric acid

Scope: This SOP describes a low-flow (minimal drawdown) technique used for groundwater sample collection. Procedures outlined in this SOP are intended to provide general instruction for groundwater sampling activities. Field personnel should consult the project work plan for additional information.

Discussion: Contaminant studies account for interaction between the mobile aqueous and immobile solid phase. The mobile, reactive solid phase (colloidal-size particles) is not accounted for and may be present in sufficient mass, possess high sorption reactivity, and remain stable in suspension and thus serve as an important mechanism to facilitate contaminant transport. Collection and processing of groundwater samples is required to determine the significance of collodial-size particles.

Colloidal-size particles (secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria) are reactive particles that have been shown to be mobile and may be required to be included in monitoring programs to identify the total mobile contaminant loading (dissolved + naturally suspended particles) at a site.

Conventional sampling methods (purging 3 to 5 well volumes) can cause an increase in turbidity, thus affecting the sample quality. Filtering to decrease turbidity of the sample may remove contaminant-associated mobile particles, thus artificially biasing contaminant concentrations low.

Purging is performed to remove water in the casing for the following reasons: oxygen concentration gradient between the top of the water column at the air interface to the bottom of the water column; loss of volatile compounds up the water column; leaching from or sorption to the casing or filter pack; chemical changes due to clay seals or backfill and surface infiltration. Low-flow purging minimizes mixing between the overlying stagnant casing water and water within the screened interval.

Low-flow refers to the velocity of water from the pore water of the formation, through the well screen and into the pump intake. It does **not** necessarily refer to the flow rate of water discharged at the surface. Flow rates of 0.1-0.5 L/min (0.026-0.13 gpm or 100 mL/min-500 mL/min) are typically used. If the pump intake is located within the screened interval, most of the water pumped will be drawn directly from the formation with little mixing of casing water or disturbance to the sampling zone.

Advantages of low-flow purging include:

- Representative samples (dissolved and colloid-associated).
- Minimal disturbance of the sampling point.
- Less operator variability; greater operator control.
- Reduced stress on the formation.
- Less mixing of stagnant casing water with formation water.
- Reduced need for filtration and less time for sampling.

- Smaller purging volume decreasing waste disposal costs.
- Increased sample consistency; reduced artificial sample variability.

References: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, *Ground Water Issue: Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, EPA/540/S-95/504, April 1996.

Minnesota Pollution Control Agency, *Groundwater Sampling Guidance: Development of Sampling Plans, Protocols and Reports*, January 1995.

New Jersey Department of Environmental Protection and Energy, *Field Sampling Procedures Manual*, May 1992.

U.S. Environmental Protection Agency-Region IV, *U.S. EPA Environmental Compliance Branch Standard Operating Procedures and Quality Assurance Manual*, February 1, 1991.

Equipment: Pump
Plastic graduated cylinder
Field measurement equipment
Pre-cleaned, pre-preserved sample containers

Selection of Sampling Equipment:

Factors to consider in selection of appropriate sampling equipment for a project should be based on technical performance of the equipment (e.g. how the equipment affects the chemistry of the water sample), and on how well the equipment will perform for the project.

Procedure:

1. Determine the order in which the wells should be sampled. Typically, sampling order should proceed from the cleanest well to the most contaminated. When no historical water quality data are available, sample background wells first, followed by the farthest downgradient wells. The wells expected to be most significantly contaminated should be sampled last. Sampling order is not as critical when a peristaltic pump is used as the pump tubing is replaced after each use.

2. Obtain the following information prior to the sampling event:

   a. Well depth. If not previously measured, determine by subtracting the distance between ground surface and top-of-casing (stick-up) and add this distance to the installation screen depth.

   b. Screen length.

c. Depth to bottom of screen and depth to top of screen from top-of-casing. Using this information, determine the depth to the midpoint of the well screen.

3. Record the condition of the monitoring well in the field notes. Additional information may be required for documentation before, during, and after groundwater sampling. Refer to SOP 10-3 for additional information.

4. Determine static water level using either SOP 18-3 or 18-4. Record in the field notebook. Minimize disturbances of the stagnant water column during water level measurement.

   Water levels are measured prior to and during a groundwater sampling event for the following reasons:

   - To assess whether the static water column length is sufficient to allow purging and sampling to proceed in a normal manner provided that drawdown is moderate.
   - To select the depth to which the pump intake or other purging or sampling device should be lowered.
   - To monitor the water level during purging and sampling and determine the optimum pumping rate to minimize drawdown.
   - To determine groundwater flow direction.

5. Rinse reusable sampling equipment with deionized water before inserting the equipment into the monitoring well.

6. Calibrate field measurement equipment as required by the project work plan.

7. Note the depth to the top and bottom of the well screen (if known) from top-of-casing. Depth of the well should **not** be measured prior to purging as this may cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure the well depth after sample collection. Compare the static water level to the depth to the top of the screen. If the water level is above the screen, insert the pump intake to the middle or slightly above the middle of the screened interval. If the water level is across the well screen, place the pump at the top of the water column.

8. Slowly insert sampler into the well to the desired depth and begin to purge at a rate (0.026-0.13 gpm or 100 mL/min-500 mL/min) that will minimize drawdown (<0.1 m or <0.33 ft). Monitor drawdown during purging using an electric tape. Make adjustments to stabilize the flow rate as soon as possible.

   When purging wells screened in low-permeability formations (<0.1 L/min recharge), lowering of the water level can cause cascading of water into the well if the purge rate is greater than the recovery rate of the well. Cascading of water into the well can accelerate alteration of the

water. Cascading should be kept to a minimum by not drawing the water level in the well below the top of the screen. If the water level is already at the top of or within the well screen, select a purging rate that results in minimum drawdown while allowing the well to be purged in a reasonable length of time .

Record purge start time in the field notebook. Use a plastic graduated cylinder or beaker to monitor the pumping rate and a 5-gallon bucket to monitor the volume of water purged. Dispose of purge water in accordance with the project work plan.

9. If drawdown is excessive during low-flow pumping, and the low-flow method is not feasible without dewatering the stored water in the well casing, the following procedure should be used:

   a. Pump the well down to the maximum extent possible with the pump set at the existing setting.

   b. Allow the pumping rate to increase to approximately 1 gpm to maximize removal of stored water in the well casing. Drawdown should not proceed below the top of the pump.

   c. If a sustained pumping rate can be achieved with drawdown not exceeding the depth to the top of the pump, continue pumping until 3 stored casing volumes have been excavated. Collect samples for field and laboratory analysis.

   d. If a sustained pumping rate cannot be achieved and the monitoring well is evacuated, shut the pump off and allow the well to recover. When the well has recovered to the point that there is a sufficient volume of water stored, restart the pump and collect samples for field and laboratory analysis.

10. Monitor water quality parameters (pH, temperature, specific conductance, Eh, dissolved oxygen, and turbidity) every 3 - 5 minutes during purging to check for stabilization. These parameters should be recorded in conjunction with time, drawdown, flow rate, and volume pumped. Temperature and pH commonly have the same signature between stagnant casing water and formation water, but should be measured. Turbidity is a very conservative parameter and will require longer purge times for stabilization. Stabilization is reached when at least 3 parameters are stable for 3 successive readings using the following criteria:

   - ±0.1 for pH
   - ±3% for specific conductance
   - ±10 mV for redox potential
   - ±10% for dissolved oxygen and turbidity

   If stabilization of 3 field parameters is not achieved after 3 stored casing volumes have been evacuated, a field decision must be made to either continue purging or to collect the samples. If it is determined that significant stabilization can be achieved, continue purging until stabilization occurs or until it is determined that a reasonable effort has been made to maximize stabilization.

If the monitoring well is sampled repeatedly (quarterly, annually, etc.) for assessment of temporal variations in water quality with time, the pump should be set to the same depth, and purged at approximately the same rate and for the same volume of water during each subsequent sampling event. If the same purging criteria does not result in stabilization in subsequent sampling events, consider the following:

- Groundwater chemistry has changed over time.
- The monitoring well may need rehabilitation (re-developed, replaced, etc.).
- Errors in field measurements may have been made during one or more sampling events.
- Collect a set of samples at the normal purging time and also collect time-series samples to compare with changes in field parameters.

It may not be possible in certain situations to reach stabilization due to:

- Non-uniform distribution of chemical and physical parameters in the water-yielding zone(s) being monitored.
- Previously undetected coalescing plumes.
- Multiple water-yielding zones screened by the monitoring well(s).
- Leaky confining layers, perched zones, etc. nearby.

11. Record field parameters (pH, temperature, specific conductance, Eh, turbidity, and dissolved oxygen) after stabilization.

12. Fill required sample containers in accordance with the procedures described in SOP 10-10. Record the type of bottle filled, preservatives added, and time and date of collection in the field notebook. Sample should be collected in the following order:

    a. Field Parameters
    b. Volatile Organics
    c. Semi-Volatile Organics (includes samples for pesticides, herbicides, and PCBs)
    d. General chemistry parameters
    e. Metals

    Refer to project work plan for sample requirements.

13. Decontaminate the equipment after each use in accordance with procedures described in the equipment- specific SOPs.

Scope: This document provides guidance for proper documentation of groundwater sampling activities.

Reference: Minnesota Pollution Control Agency, *Groundwater Sampling Guidance: Development of Sampling Plans*, Protocols and Reports, January 1995.

BTU.S. Environmental Protection Agency-Region IV, *U.S. EPA Environmental Compliance Branch Standard Operating Procedures and Quality Assurance Manual*, February 1, 1991.

BTU.S. Environmental Protection Agency Ground Water Issue, *Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures*, EPA/540/S-95/504, April 1996.

Procedure:

1. A number of forms have been developed for documentation of field data and sampling activities. These forms provide a means to verify whether or not the project required protocol was followed during a number of key steps in a groundwater sampling event. The chronological design of the forms allow them to be used as a field task check list to assure the tasks are completed in the proper order. Additional documentation of field activities should be logged in the field notebook.

2. The groundwater documentation forms are divided into seven sections: project header, inspection, static water level measurement, well purging, field analysis, sample collection, and sampling personnel. These sections will be customized to meet specific project requirements, but the layout of the sections will remain consistent.

3. To fully implement the protocol verification feature of the forms, complete all entries before leaving the sampling point. This includes filling in all appropriate blanks and circling or checking all "yes" or "no" choices on the forms. Incomplete entries may result in an ambiguous record of what transpired in the field.

4. Complete comment fields when an event occurs that could impact data or the validity of data.

5. Ditto marks or arrows may be used in any column to indicate "same as above". "N/A" or a horizontal line may be used to indicate "not applicable".

6. Forms should be completed as follows:

   a. Project header

      Record the following information:

      - Project name, number and location.
      - Sampling event (1st quarter, 2nd quarter, etc.).

- Well number.
- Well type (flush mount, well diameter, etc.).
- Key number.

b. Inspection

- Document well conditions.
- Note well maintenance issues and/or any repairs made.
- Document additional information in field notes.

c. Static water level

Record the following information:

- Depth to water.
- Type of measuring equipment used.
- Date and time the reading was taken.
- Method used to decontaminate the measuring equipment.

d. Well purging

1. Prior to groundwater sample collection, an appropriate volume of water must be removed from the well to assure that the chemistry of the sample is representative of the actual groundwater chemistry. When using the conventional purge method, record the following information:

   - Calculation of 3 casing volumes
   - Actual gallons purged
   - Purge method
   - Equipment number
   - Water quality stabilization readings (if required) and time of measurement
   - Date and time of well purging

2. When the low-flow technique is used, record the following information:

   - Purge method
   - Date and time of well purging
   - Measured well depth, screen length, and depth to screen midpoint
   - Drawdown, pumping rate, volume pumped, pH, temperature, specific conductance, Eh, turbidity, and dissolved oxygen at 3 - 5 minute intervals to monitor for stabilization

e. Field Analyses

- Record equipment calibration data.

- Record results of calibration checks.
- Record results of groundwater analysis and date and time taken.

f. Sample Collection

- Record groundwater appearance
- Record date, time, and sampling method
- Record the number, size, and type of bottles.
- Note whether or not the sample was filtered and indicate the preservative used.
- Document QC sample collection (duplicate, MS/MSD)
- Record the chain-of-custody number associated with the samples

g. Sampling personnel

Include signature and date on bottom of form.

fTC&h **STANDARD OPERATING PROCEDURE** **SOP10-06**
Groundwater Sampling Collection Using Peristaltic Pump
06/10/1998; Revised 02/18/00

Scope: The following SOP outlines the technique to be used to acquire groundwater samples from monitoring wells using a self-priming suction lift pump. This SOP is intended to provide general instruction. Consult the equipment manual and project work plan for additional information.

References: New Jersey Department of Environmental Protection and Energy, *Field Sampling Procedures Manual*, May 1992.

U.S. EPA Environmental Compliance Branch, *Standard Operating Procedures and Quality Assurance Manual*, February 1, 1991.

Operator's Manual, Masterflex Easy-Load Pump Head Model 7518 Series, Cole-Parmer Instrument Co.

Operating Manual, Masterflex L/S Portable Sampling Pump Drive Model No. 7570-10, Cole-Parmer Instrument Co.

Procedure:

1. Check pump tubing for cracks or leaks. Replace if necessary.

2. Feed a new piece (approximately 3 feet in length) of the flexible of tubing through the rotor opening.

3. Lock the tubing (approximately mid-length) in place by pushing the loading lever 180° to the right. Allow the discharge end of the tubing to extend into a bucket.

4. Release the 2 tubing retainers from the retracted position by pushing them slightly into the body, then downward and firmly against the tubing. Adjust as necessary.

5. Unroll and cut off a new piece of rigid tubing with length equal to the well depth plus an additional 5 to 10 feet.

6. Insert the free end of the rigid tubing into the well just below the water surface leaving the excess extending out of the well.

7. Secure the rigid tubing to the well casing or other suitable object to prevent the tubing from dropping into the well should the tubing come loose from the pump head.

8. Attach the rigid tubing to the piece of flexible tubing connected to the pump.

9. Turn on the pump to produce a vacuum on the well side of the pump head and begin purging. Observe the pump direction to ensure that a vacuum is being applied to the sample/purge line.

10. Refer to SOP 10-1 for guidance on standard groundwater sampling. Refer to SOP 10-2 for guidance on low-flow groundwater sampling.

11. Pump tubing must be replaced after each use. Place used tubing in a plastic trash bag for disposal. Wipe the pump unit down with a Liquinox® soap and water solution followed by a deionized water wipe.

fTC&h **STANDARD OPERATING PROCEDURE** **SOP 10-07**
Groundwater Sampling Collection Using Bailer
11/19/1996; Revised 11/19/1996

Scope: This SOP outlines the technique required for groundwater sample collection using a single check valve bailer. Procedures outlined in this SOP are meant to provide general instruction for groundwater sampling activities. Field personnel should consult the project work plan for additional information.

References: New Jersey Department of Environmental Protection and Energy Field Sampling Procedures Manual, May 1992.

Procedure:

1. Attach a braided polypropylene line to the bailer. Rinse the bailer thoroughly with deionized water prior to use.

3. Lower the bailer into the monitoring well slowly until it contacts the water surface.

4. With a minimum of surface disturbance, allow the bailer to fill with water.

5. Slowly raise the bailer to the surface. Avoid contact of the bailer line to the well casing and/or ground. Transfer the water into a container to measure the volume of water being evacuated. Three bailer volumes of sample water must be rinsed through the bailer prior to sample acquisition.

6. Attach a bottom emptying device (stopcock with an attached sample line on a Teflon bailer or a draft valve and sample line on a disposable bailer). Insert the valve (in the open position) into the bottom of the bailer, pushing the check valve up and supplying water to the sample line. Close the valve after insertion.

7. At the completion of sample collection, decontaminate Teflon sampling bailers with a soap and water wash followed by a deionized water rinse. Diposable bailers should be discarded.

Scope: This SOP outlines procedures for the collection of groundwater quality control samples. These samples may include equipment blanks, atmosphere blanks, filter blanks, duplicates, and matrix spike samples. Refer to the project work plan for specific information regarding the QC samples required.

References: Minnesota Pollution Control Agency, *Groundwater Sampling Guidance: Development of Sampling Plans*, Protocols and Reports, January 1995.

Procedure:

A. Equipment Blanks

Equipment blanks are collected to evaluate if the investigative groundwater samples may have been contaminated through contact with the sampling equipment. An impacted equipment blank sample may indicate inadequate decontamination procedures, or that parts of the sampling equipment (e.g., pump tubing) may have become contaminated through continued use and should be replaced. Equipment blanks are typically collected at a rate of 1 equipment blank per 10 investigative samples.

Equipment blank samples are collected by passing deionized water through the sampling equipment using the same procedure used to collect the investigative groundwater samples.

1. Prior to collecting the equipment blank sample, be sure that the sampling equipment has been decontaminated following standard procedures.

2. If a pump is used for sample collection, prepare the equipment blank by pumping deionized water from the final rinse container into the appropriate sample containers.

3. If a bailer is used for sample collection, pour deionized water (with as little agitation as possible) into the top of the bailer. The length of time the blank water has contact with the bailer should simulate the length of time that an actual groundwater sample would contact the bailer. If a disposable bailer is used, do not rinse it with deionized water prior to collection of the equipment blank.

4. Equipment blanks are analyzed for the same parameters as the groundwater samples and therefore an identical "set" of bottles should be filled. The bottles should be filled in the same order required for the groundwater samples. If field filtering is required, follow the procedures described in Section C below.

5. Standard decontamination procedures should be followed after collection of the equipment blank.

B. Atmosphere Blanks

Atmosphere blanks are collected during sampling events where dedicated equipment is used to collect groundwater samples (such as Well Wizard dedicated pumps).These samples are used to determine if contact with ambient air has impacted the groundwater samples.

1. Collect an atmosphere blank sample by pouring deionized water into the appropriate sample containers at the same rate and duration that it takes to collect a groundwater sample. Atmosphere blanks are analyzed for the same parameters as the groundwater samples and therefore an identical "set" of bottles should be filled.

2. The bottles should be filled in the same order and preserved in the same manner required for the groundwater samples. If field filtering is required, follow the procedures discussed in Section C below.

3. Atmosphere blanks should be collected at a rate of one per 10 investigative groundwater samples.

C. Filter Blanks

Filter blanks are collected when groundwater samples are filtered onsite. These samples are used to evaluate the impact of the filtering equipment on the groundwater samples.

1. Collect a filter blanks by running deionized water through decontaminated filtering equipment fitted with a new filter. Do not pass the sample through the sampling equipment. The filter blank is used to determine whether the filtering equipment has affected the groundwater sample, independent from the sampling equipment

2. Filter blanks will be analyzed for the same parameters as the filtered groundwater samples and therefore an identical "set" of bottles should be filled. The bottles should be filled in the same order required for the groundwater samples.

3. Filter blanks should be collected at a rate of one for every 10 investigative filtered groundwater samples.

D. Field Duplicates

Field duplicates are collected as a check of sampling and analytical reproducibility.

1. Sample duplicates should be collected using the same procedure as for the investigative samples. Sample duplicates will be analyzed for the same parameters as the investigative groundwater samples and therefore an identical "set" of bottles must be filled.

2. The parameter dictated bottle order should be followed, however the sample duplicate bottles for specific parameter analysis should be filled immediately after the "primary" groundwater sample bottles. Following this procedure, the "primary" sample and sample duplicate bottles are filled alternately, and the parameter dictated sampling order is maintained.

3. Field duplicates are typically collected at a rate of one for every 10 investigative groundwater samples.

E. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD samples are used to evaluate laboratory precision and accuracy. MS/MSD samples are typically analyzed by laboratory as part of their QA/QC program. To insure that project specific matrix spike analysis is performed, it must be requested from the analytical laboratory. Consult the project work plan for sample volume requirements. Typically, triple the normal sample volume is required for analysis.

MS/MSD samples are collected in the same manner as field duplicates. Refer to Section D of this SOP.

F. Trip Blanks

Trip blanks, consisting of deionized water in sealed 40 mL glass vials, are prepared by the laboratory prior to the sampling event and are included in each sample shipping container. Trip blanks must be kept with the investigative samples throughout the sampling event and shipment to the laboratory. Trip blanks are used to assess potential contamination of samples due to compound migration during sample handling, shipment, and storage.

Scope: This SOP outlines the technique required for collecting groundwater samples from monitoring wells using a positive displacement, gear-drive, electric submersible pump. This SOP is to be used in conjunction with other SOPs for the collection of water samples for analysis of specific parameters as stated in the project work plan.

Discussion: The Fultz® pump is a small 24-volt DC submersible positive displacement pump suitable for purging and sampling most 2-inch diameter wells. The pump is manufactured by Fultz Pump, Inc., P.O. Box 550, Lewiston, PA 77044, U.S., 717-248-2300. The pump has a diameter of 1.75 inches, a length of 9.16 inches, and weighs approximately 2.5 pounds. The pump housing is constructed of 304 stainless steel. The inlet screen is 60 mesh stainless steel, rotor is Teflon®, housing seal is viton, and motor shaft seal is carbon. The pump houses a high-efficiency electric motor and Teflon® gears (rotors). Water is pulled through the fine-mesh stainless steel screen on the pump head by the meshing rotors and is positively displaced through the discharge hose. The discharge hose is constructed of 0.5 inch I.D. Teflon® tubing. The discharge tubing and power cable are together shielded with polyethylene shrink-wrap.

Power to the pump is supplied by an internal power pack comprised of four 6-volt gel cell batteries. The manufacturer also offers an external power pack, containing the same array of batteries as the internal supply, and a 24-volt DC generator as optional power sources. The pumps can operate at higher rates and for longer periods of time when powered either with the generator or with two 12-volt car or motorcycle batteries connected to provide 24 volts.

The operating performance data indicate the Fultz® Model SP-300 will deliver a maximum rate of 1.1 gpm at 150 feet head. The pump controls allow the operator to dial down the amperes to pump less than 0.013 gallon/minute (<50 mL/minute). The pump size, construction materials, and low flow capabilities make this pump ideal for groundwater sampling using low flow methodology.

The following is a list of switch functions found on the control panel of the Fultz® pump:

ON	Supplies power from selected power source to pump motor.
OFF	Turns pump off.
INTERNAL	Selects the internal battery array as the power source for the pump.
EXTERNAL	Selects an external power source. Source must be plugged into front panel at exterior source plug.
FORWARD	Selects forward operating mode, used to pump water from the source.

REVERSE Selects reverse operating mode, used to empty water from hose through pump head and to flush silt from pump screen, when clogged. Power to the pump should be off before the direction of pump is changed to prevent damage to unit or fuse.

References: Instruction manual for the Fultz® Pump, Inc.

Ground-Water Data–Collection Protocols and Procedures for the National Water-Quality Assessment Program: Collection and Documentation of Water-Quality Samples and Related Data, Michael T. Koterba, et al., U.S. Geological Survey, Open-File Report 95-399, 1995.

Procedure:

1. Rinse the pump with thoroughly with deionized water prior to inserting it into the monitoring well.

2. Follow the procedure outlined in SOP 10-2 (steps 1 through 5). This procedure refers to the necessary tasks and data to be measured and recorded prior to sampling (i.e. order of sampling, monitoring well condition, static water level measurement, etc.).

3. Connect the power cable to the 24 VDC (volts direct current) power supply and turn the Voltage/Current Meter to "ON - VOLTAGE." 24 VDC is required to operate the pump. If less than 24 VDC is displayed, replace the DC power source.

4. Check pump head to make sure pump and electrical connections are secure.

5. Lower pump into the screen.

6. Power the pump on and make sure REVERSE/FORWARD switch is in FORWARD position. If the polarity of the power connection is reversed, the amp meter will deflect to the left and the pump will be running opposite of the selected direction. Make the appropriate change.

7. Follow steps 8 through 12 in SOP 10-2. During normal operating conditions, the pump should pull no more than 1.5 to 2.0 amps. Newly replaced rotors may temporarily pull slightly more amps. Check amp meter on control panel to make sure pump is operating in this normal range.

8. After completing the sampling, remove the pump from the well and reverse the motor to empty the pump and hose of all contained water. The pump should be switched off as soon as the last water is discharged, as running the pump dry may damage the rotors. This water should be collected and handled appropriately.

9. Decontaminate the pump between each use. Decontamination should consist of cleaning the pump casing, hose, and cables with a mild laboratory grade detergent solution, followed by a

10 - 15 gallon flush of deionized water through the pump. Follow with a deionized water rinse of the outside of the pump.

frc&h **STANDARD OPERATING PROCEDURE** **SOP 11-03**
Field Measurement of pH by Electrode
05/18/1998; Revised 05/18/1998

Scope: This SOP outlines the technique required for the accurate field measurement of pH using the Orion Model 260 Meter and Model 9107 WP electrode.

References: Orion Model 260 Waterproof pH meters Instruction Manual
Orion Model 9107WP pH Electrode Instruction Manual

Equipment: Orion Model 260 Meter
Orion Model 9107WP pH electrode (Probe)
pH Buffer Solutions (pH = 4.01, 7.00 and 10.01)
Probe preservation solution
Distilled or Deionized Water

Procedure:

A. Electrode Preparation

1. Rinse the exterior of the probe with deionized water to remove any salt deposits.

2. Shake the electrode (like a clinical thermometer) to remove air bubbles.

3. Connect electrode to the meter.

B. Self-Diagnostics Checkout

1. Hold down the RUN/ENTER key while pressing the ON/OFF key to turn the meter on.

2. The meter will perform self-diagnostic tests and do an internal slope adjustment. The slope will be set to a default of -59.2 mV/pH and E_0 to a default of 0 mV. The temperature is not reset.

C. Calibration

Calibration serves two functions: (a) determines if the electrode is functioning properly, and (b) calculates the proper slope for accurate pH measurements. The Orion pH meter automatically performs 1 or 2 point calibrations (with automatic temperature compensation to 25°C), or can be calibrated manually (the temperature of the standards must be entered). Automatic calibration using calibration standards of 2.00, 4.01, 7.00, or 10.01 is preferred. To calibrate the instrument manually or with standards different than those listed above, consult the instruction manual.

1. Press the ON/OFF key to power the meter on. The stored value of the pH slope will be displayed, followed by the stored E_0 value. If the *LoBat* indicator remains on, replace the batteries prior to use.

3. Choose 2 buffers which most closely reflect anticipated pH values. A pH 7.00 buffer is recommended and with EITHER a pH 4.01 or pH 10.01 buffer.

4. Press the CAL key until the *AutoCal* and *TEC* indicators are lit.

5. Rinse the electrode with deionized water, gently shake to remove water from the end of the probe and immerse into the first standard.

6. Press the RUN/ENTER key. The AR display indicator will flash and a mV value will be displayed. The AR display indicator will stop flashing when the meter has accepted the buffer. Ct2 will appear on the display.

7. Rinse the electrode with deionized water, gently shake to remove water from the end of the probe and immerse into the second standard.

8. Press the RUN/ENTER key. The AR display will stop flashing when the meter has accepted the buffer.

9. The electrode slope will be displayed in mV/pH. The slope must be between 92-102% to ensure that the probe performance meets the manufacturers specification. Record the slope value in the field notebook.

10. Press the RUN/ENTER key. The E_o of the electrode will be displayed in mV. The value should read between +30 and - 30mV if the probe is operating correctly.

11. If Error message E3 appears, check the buffers and electrode, rinse the electrode, immerse in a fresh aliquot of standard, and press the RUN/ENTER key *twice* to restart the calibration. Consult the pH meter instruction manual for further assistance.

D. Sample Preparation - Soils

1. To 25g of soil in a 125 mL plastic bottle, add 25 mL deionized water; cap and continuously swirl for 1 - 2 minutes. Other soil:water ratios are allowed if working with hygroscopic soils or other problematic soil matrices.

2. Allow the suspension to settle prior to measurement (up to 1 hour). Decant liquid from the settled solids prior to pH measurement.

E. Sample Measurement

1. Prior to sample measurement, confirm calibration by checking the 4.01, 7.00 and 10.01 buffer solutions with the calibrated instrument. Measured values should agree within ±0.1 su or recalibration should be performed. Rinse the probe with distilled or deionized water before and after each measurement.

2. Immerse pH probe in the sample and press the RUN/ENTER key.

3. Record the pH and temperature of the sample when a stable reading is obtained.

4. Remove the probe from the sample and rinse well deionized water.

4. Check the instrument for drift after every 2-4 hours (*or according to the site specific work plan*) by measuring the standard closest in pH to the samples being measured. Record in the field notebook. Recalibrate the instrument if the reading deviates more than 0.10 pH units from certified value.

5. If the instrument does not calibrate within 0.1 pH units, consult the meter and probe instruction manuals. Recalibrate the instrument with a back-up probe if necessary.

F. Electrode Storage

For storage up to one week, use Orion electrode storage solution. A temporary solution can be made with 1 gram of KCl added to 200 ml of pH 7 buffer. Do not store the electrode in deionized water as that will shorten the life of the probe. If the probe will not be used for periods greater than one week, clean the electrode as directed in the manual, secure the protective cap and store dry.

G. Electrode Maintenance

Refer to the pH electrode instruction manual for cleaning and maintenance instructions.

H. Buffer Solutions

Solutions stored for more than one year should be checked against fresh buffers. Deterioration is greatest for high pH buffers.

For all buffer solutions, pH changes with temperature. During calibration, the temperature of the buffer should be noted and the corresponding pH value should be used to calibrate the meter. Table 1 presents pH versus temperature for the three standard buffers used by FTC&H personnel for calibrating the pH meters. The buffer solutions should be stored between 5°C to 45°C.

Table 1 • Temperature Correction for pH Buffer Solution for Calibration

	pH 4.01 ± .01@25°C Red Potassium Hydrogen Phthalate Buffer, 0.05 Molar	pH 7.00 ± .01@25°C Yellow Sodium and Potassium Phosphate Buffer, 0.05 Molar	pH 10.01 ± .01@25°C Blue Sodium Carbonate Buffer, 0.025 Molar
°C	Calculated pH	Calculated pH	Calculated pH
0	4.00	7.12	10.32
5	4.00	--	10.25
10	4.00	7.06	10.18
15	4.00	--	10.12
20	4.00	7.02	10.06
25	4.00	7.00	10.01
30	4.01	6.99	9.97
35	4.02	6.98	9.93
40	4.03	6.97	9.89
45	4.04	--	9.86
50	4.06	--	9.83
60	4.09	6.98	--
70	4.13	--	--
80	4.16	7.04	--
90	4.19	7.09	--

Caution: pH 10.01 Blue Buffer -- absorption of atmospheric CO_2 will lead to degradation of product.

Scope: This SOP outlines the technique required for the accurate field measurement of specific conductance using the Orion 128 Model Conductivity Meter.

References: Orion Model 128 Waterproof Conductivity Meter Instruction Manual

Equipment: Orion Model 128 Specific Conductance Meter
Specific Conductance Standards (147 μMHOS, 1413 μMHOS, 2767 μMHOS)
Deionized Water
Field Notebook

Procedure:

A. Electrode Preparation

1. Connect the conductivity probe to meter.

2. Rinse probe with distilled or deionized water.

B. Meter Inspection

1. Press the ON/OFF button to turn the meter on. All display annunciators will illuminate briefly.

2. If the low battery (LoBat) indicator remains on, the meter has a maximum of 16 hours of power remaining. The instrument will remain accurate until the batteries are completely dead, but the batteries should be replaced as soon as possible.

   a. Replace all of the batteries with disposable AA alkaline batteries.
   b. Be sure that the instrument is turned off before opening battery compartment.
   c. Consult the instruction manual for assistance.

C. Calibration

The Orion 128 Model specific conductivity meter is factory calibrated. However, three standards covering the range of conductivities anticipated in the field must be measured to insure that the instrument is operating properly. The instrument automatically compensates for changes in temperature. The readout is adjusted to 25°C. The conductivity is reported in microSiemans per centimeter(μS/cm) and milliSiemans per centimeter (mS/cm) which are equivalent to micromhos (μmhos/cm) and millimhos (mmhos/cm).

The calibration solutions are prepared by KAR Laboratories, Inc.. These solutions should be replaced every 3 months. Available standards for use are 147, 1413, and 2767 μmhos/cm.

1. Rinse the cell in deionized or distilled water and blot dry.

2. Select standards representative of the water samples to be measured.

3. Immerse the cell into the standard solution.

4. Use the selector switch to select the appropriate measurement range. (If *OFL* is displayed, select the next higher measurement range.)

5. Record the standard used, the conductivity readout, and the temperature of the standard in the field notebook. If the instrument is operating properly, the meter should read within 2% of the actual value of the standard.

6. If the reading is outside the 2% error window:

   a. Measure other standards to determine if the electrode, or a specific standard is in error.

   b. If the instrument exceeds the 2% margin of error with other standards, replace the probe.

D. Sample Analysis

1. Rinse the probe with deionized water, followed by a rinse with the sample to be measured.

2. Immerse the probe into the sample. Use the selector switch to select the appropriate measurement range. (If *OFL* is displayed, select the next higher measurement range)

3. Record the conductivity of sample when a stable reading is obtained.

4. Remove the probe from the sample and rinse well with deionized water.

E. Calibration Check

1. Check the instrument for drift every 4 hours by measuring the standard closest to the conductivity of the samples being measured. Even though the instrument cannot be calibrated, this check documents the integrity of the instrument and the probe. (The literature indicates that a conductivity instrument should be recalibrated if the reading deviates more than 10 units for standards <1,000 umhos and more than 100 units for standards >1,000 μmhos/cm).

Scope: This SOP outlines the technique required for the accurate field measurement of turbidity using the Cole-Parmer Field Turbidimeter Model 8391-50.

Equipment: Cole Parmer Field Turbidimeter Model 8391-50
Methanol
Sample cuvette
Turbidity standards (.5 NTU and 10 NTU) - DO NOT ALLOW TO FREEZE.
Distilled or Deionized Water
Field Notebook
Kimwipes

Procedure:

A. Primary Calibration

This procedure should be performed quarterly or any time a NEW sample cuvette is put into use.

1. Turn on the turbidimeter and allow to warm up for 5 minutes.

2. Set the range switch to 0-20.0 NTU and prepare the cuvette with the 10 NTU primary standard.

3. Insert the cuvette into the test well, align and cover with the light shield.

4. Adjust the SET/CAL control until the display reads 10.0.

5. Remove the primary standard and replace it with the sealed 10.0 NTU secondary standard. Align the cuvette and cover with the light shield.

6. Record the NTU value of the sealed standard on the label. This value will now be used for daily calibration.

7. Pour the 10 NTU standard out of the sample cuvette and shake out the remaining droplets. Rinse twice with distilled water and wipe the outside of the cuvette with a Kimwipe moistened with a small amount of methanol.

8. Change the range switch to 0-2 NTU range and prepare the sample cuvette with the 0.5 NTU standard.

9. Insert the cuvette into the test well, align and cover with the light shield.

10. Adjust the ZERO NTU adjust screw so that the display reads 0.500. Make sure the reading has stabilized.

11. Remove the primary standard and replace it with the sealed 0.5 NTU secondary standard. Align it and cover with the light shield.

12. Record the NTU value of the sealed standard on the label. This value will now be used for daily calibration.

13. Set the range switch to 0-20.0 NTU. Insert the 10 NTU sealed standard, align and cover.

14. The SET/CAL adjust may require a slight adjustment. Set the meter to read the calibrated value of the sealed standard that was recorded in step 6.

B. Daily Calibration

1. Turn on the turbidimeter and allow it to warm up for 5 minutes.

2. Set the range switch to 0-20.0 NTU.

3. Insert the 10 NTU sealed secondary standard cuvette into the test well, align and cover with the light shield.

4. Using the SET/CAL control, adjust the display to the calibrated standard value obtained during primary calibration.

5. Remove the 10 NTU standard and set the range switch to 0-2.

6. Insert the 0.5 NTU sealed secondary standard into the test well, align and cover with the light shield.

7. Using the zero NTU adjust screw, set the display to the calibrated standard value obtained during primary calibration.

8. Remove the 0.5 NTU standard.

9. Set the range switch back to 0-20.0 NTU, insert the 10 NTU sealed secondary standard, align and cover.

10. The SET/CAL adjust may require a slight adjustment. Set the meter to read the NTU value of the sealed secondary standard. The turbidimeter is now calibrated and ready for sample measurements.

C. Sample Analysis

1. After calibrating the turbidimeter, set the switch to 0-20.0 NTU range.

2. Rinse the cuvette twice with the sample to be tested and then slowly fill the cuvette to the alignment mark. Refill if air bubbles form on the walls of the cuvette.

3. Cap the cuvette and carefully wipe the outside of the sample cuvette with a Kimwipe moistened with a small amount of methanol to remove any fingerprints or moisture.

4. Insert the cuvette into the test well, align and cover with the light shield.

5. Once the reading has stabilized, record in the field notes.

6. If the reading is outside the 0-20.0 NTU calibration range, adjust the range to the appropriate setting (0-2 NTU or 0-200 NTU), allow the sample to stabilize and record the reading in the field notes.

7. Rinse the cuvette thoroughly with deionized water and cap upon completion of testing.

D. Quality Control

1. A sample duplicate should be run at a frequency of 1 per 10 investigative samples. Duplicate readings should agree within ±10%. If values fall outside this range, recalibrate the turbidimeter and reanalyze.

Scope: This SOP describes the technique required for the accurate field determination of dissolved oxygen (DO) in water using the YSI Model 51B or YSI Model 55 Dissolved Oxygen Meter.

Equipment: YSI Model 51B or YSI Model 55 Dissolved Oxygen Meter

Procedure:

YSI Model 51B

A. Instrument Calibration

Note: Instrument calibration should be performed daily prior to sample measurement.

1. Place the meter in the intended operating position (vertical, tilted, or on its back) before preparing the meter for use. Readjustment may be necessary if the instrument operating position is changed.

2. With the meter off, adjust the meter pointer to zero using the screw in the center of the meter panel. Do not force this adjustment.

3. Switch the meter to **ZERO** and adjust the reading to zero using the **ZERO** knob.

4. Switch to **FULL SCALE** and adjust using the **FULL SCALE** knob until the meter needle aligns with 15 on the mg/L scale.

5. Attach probe to the instrument and allow 15 minutes for optimum probe stabilization and polarization before calibration.

6. Switch to **CALIB O_2** and place the probe in a partially filled BOD bottle or other small calibration bottle along with a few drops of water. The probe can also be wrapped loosely in a damp cloth taking care that the cloth does not touch the membrane. Allow 10 minutes for temperature stabilization. This step may be performed at the same time the probe is stabilizing.

7. Using the calibration (**CALIB**) knob, adjust the needle to the local altitude (600 - 650 feet above mean sea level).

B. Sample Measurement

1. Following instrument preparation and probe calibration, place the probe in the sample to be measured.

2. If a stirrer is not used, provide manual stirring by raising and lowering the probe about 1 ft. per second.

3. Allow sufficient time for the probe to stabilize to sample temperature and dissolved oxygen.

4. Switch to TEMP and read the temperature from the lower meter scale.

5. Set the O_2 SOLUBILITY FACTOR dial to the observed temperature, being sure to use the appropriate salinity index.

   Note: Less oxygen can be dissolved in salt water than in fresh water. The amount varies with the degree of salinity and the relationship can be considered linear for the range of fresh water to sea water, which corresponds to the instrument range of 0 to 20,000 mg/L chloride. Select the correct position along the instrument index scale when dialing in the temperature. Fresh water has a salinity of approximately zero.

6. Switch to READ O_2 and read dissolved oxygen in mg/L directly from the meter.

7. Rinse the probe with deionized water between sample measurements.

C. Maintenance

1. Store the probe with protective cover in place.

2. Replace the four C size batteries every six months or when "full scale" adjustment cannot be made or O_2 calibration cannot be accomplished.

<u>YSI Model 55</u>

A. Instrument Calibration

Note: Each time the YSI Model 55 has been turned off, it may be necessary to recalibrate before taking measurements. All calibrations should be performed at a temperature as close as possible to the samples being measured.

1. Ensure the sponge inside the calibration chamber is wet. Insert the probe into the calibration chamber.

2. Power the instrument on by pressing the **ON/OFF** button on the front of the instrument. Allow the dissolved oxygen and temperature readings to stabilize before proceeding. A few minutes are usually required.

3. Using two fingers, press and release the two ▲ ▼ keys at the same time.

4. Enter the local altitude in hundreds of feet at the prompt using the arrow keys to increase or decrease the altitude. (Entering the number 12 here indicates 1200 feet.)

5. When the proper altitude appears on the LCD, press the **ENTER** key once to view the calibration value in the lower right of the LCD; and a second time to move to the salinity compensation procedure.

5. At the prompt, enter the approximate salinity of the water for analysis (0 to 40 ppt). Use the arrow keys to increase or decrease the salinity compensation. When the correct salinity appears on the LCD, press the **ENTER** key.

6. Once the calibration process is complete, the only keys which will remain operational are the **MODE** key, the **LIGHT** key, and the **ON/OFF** key. To alternate between dissolved oxygen in mg/L to % air saturation press the **MODE** key. Press the **LIGHT** key to activate the back-light of the YSI Model 55. The **ON/OFF** key will power the instrument on or off.

B. Sample Measurement

1. Following instrument preparation and probe calibration, place the probe in the sample to be measured. If a stirrer is not used, provide manual stirring by raising and lowering the probe about 1 ft. per second.

2. Record the DO and temperature, allowing sufficient time for the probe to stabilize to sample temperature and DO.

C. Maintenance

1. Replace the probe membrane and KCl solution erratic readings are obtained or evidence of membrane damage occurs.

2. For correct probe operation, the gold cathode must always be bright. If it becomes tarnished, restore the cathode using the YSI Model 5680 Probe Reconditioning Kit.

3. If the silver anode becomes contaminated, remove the O-ring and membrane and soak the probe overnight in 3% ammonium hydroxide. Rinse the sensor tip and KCL reservoir with deionized water, add new KCl solution, and install a new membrane and O-ring.

4. Store the probe in the calibration chamber with a small piece of moist towel or sponge.

Quality Control:

Perform duplicate sample measurements every 10 samples. Duplicate sample readings must be within +/- 0.5 mg/l of the investigative DO reading. If the reading is outside the acceptable limits, recalibrate the instrument and reanalyze all associated samples.

Table 1 • Solubility of Oxygen in Fresh Water

Temp °C	Solubility mg/l	Temp °C	Solubility mg/l	Temp °C	Solubility mg/l
0	14.62	17	9.67	34	7.07
1	14.22	18	9.47	35	6.95
2	13.83	19	9.28	36	6.84
3	13.46	20	9.09	37	6.73
4	13.11	21	8.92	38	6.62
5	12.77	22	8.74	39	6.52
6	12.45	23	8.58	40	6.41
7	12.14	24	8.42	41	6.31
8	11.84	25	8.26	42	6.21
9	11.56	26	8.11	43	6.12
10	11.29	27	7.97	44	6.02
11	11.03	28	7.83	45	5.93
12	10.78	29	7.69	46	5.84
13	10.54	30	7.56	47	5.74
14	10.31	31	7.43	48	5.65
15	10.08	32	7.31	49	5.56
16	9.87	33	7.18	50	5.47

FTC&H **STANDARD OPERATING PROCEDURE** **SOP 11-10**

In-Line Field Measurement of Temperature, Specific Conductance, pH, Eh, and Dissolved Oxygen

05/15/1998; Revised 02/21/00

Scope: This SOP outlines the technique required for the accurate field measurement of temperature, specific conductance, pH, Eh, and dissolved oxygen using the QED MicroPurge® Flow Cell Model FC4000 or FC5000. Each unit consists of a suite of three probes with five sensors mounted together inside a flow-through cell. As groundwater is pumped through the cell (up to 2 gpm or up to 10 gpm with flow diverter), field parameters are simultaneously measured and displayed. Other measurement parameters include resistivity, total dissolved solids, and salinity.

Equipment: Sampling Pump
QED MicroPurge® Flow Cell Model FC4000 or Model FC5000
3/8-inch diameter polyvinyl discharge tubing
1/2-inch diameter polyvinyl discharge tubing
Deionized Water

Standards: Conductivity standards (147, 1413, 2767 μmhos/cm)
pH standards (4.01, 7.00, 10.01 s.u.)
Eh standards (Solution A=+234 mV, Solution B=+300 mV)

Replace solutions by expiration date on label. Store at 5°C to 45°C.

Procedure:

The flow cell meter and sonde should be thoroughly checked for proper operation prior to leaving FTC&H. This should include a check of internal calibration and adjustment as required. Procedures for internal calibration as well as other detailed operating procedures can be found in the operation manuals. The analyzer is capable of displaying the parameters in various units: temperature in °C, °F, and °K; specific conductance in μS/cm or mS/cm; pH in s.u. or mV; dissolved oxygen in mg/L or % saturation; and Eh in mV. The desired reporting unit for each parameter should be selected prior to calibration.

A. Electrode Preparation

1. Temperature/Conductivity Probe

   a. Inspect thermistor and electrodes for corrosion or fouling.

2. Dissolved Oxygen Probe

   a. Inspect membrane. Replace when the membrane covering the cell becomes wrinkled, bubbled, dirty, torn, or otherwise damaged.

   b. Check DO charge readings. Perform maintenance if readings are >75 mV or < 25 mV.

3. pH/Eh Probe

   a. Inspect probe for damage or fouling. Perform maintenance when obviously coated with oil, sediment, or biological growth.

B. Flow-cell Inspection

1. Inspect flow-cell for cleanliness. Refer to maintenance section for cleaning information.

2. Inspect O-rings and O-ring seats for damage that may prevent sealing.

C. Meter Inspection

1. Check meter for sufficient battery power.

D. Calibration

1. Dissolved Oxygen

   If water-saturated air is used as the calibrating medium, make certain that both the DO reading and the temperature have stabilized for 10 to 15 minutes before starting the calibration sequence. A wet thermistor can indicate artificially low temperature readings due to evaporation, resulting in poor temperature compensation and inaccurate readings. Calibrate at a temperature as close to that of the sample being measured as possible.

   a. Place approximately 1/8" of water or a wet sponge in the bottom of the flow cell.

   b. Place the probe end of the sonde into the flow cell. Make certain that the DO and the temperature probes are <u>not</u> immersed in the water.

   c. Wait approximately 10 minutes for the air in the calibration cup to become water saturated and for the temperatures of the thermistor and the oxygen probe to equilibrate. Make certain that the calibration cup is vented to the atmosphere.

   d. From the *Calibration Mode* menu, select *Dissolved Oxy* and then *DO %* to access the calibration procedure for percent dissolved oxygen.

e. Enter the current barometric pressure in mm of Hg.

1. Current barometric pressure can be obtained from the local weather bureau or airport. If using data from these sources, be aware that the number is corrected to sea level. Determine the uncorrected atmospheric pressure using the following equation:

$$BP_{uc} = BP_c - 2.5(A/100)$$

Where BP_{uc} = uncorrected barometric pressure
BP_c = barometric pressure corrected to sea level
A = local altitude, feet above sea level

2. Barometric pressure can be estimated using the following equation:

$$BP = 760 - 2.5(A/100).$$

3. Table 1 presents barometric pressure (mm of Hg) at various elevations.

f. Press <*Enter*> and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

g. Observe the readings for percent dissolved oxygen (*DO%*) and Temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>.

h. When the calibration has been accepted, press any key to return to the data display and press <*Esc*> to return to the *Calibration Mode* menu.

i. Rinse the sonde with deionized water and allow to dry.

2. Specific Conductance

a. Place approximately 300 mL of conductivity standard in the calibration cup. The conductivity standard chosen for calibration should be within the same conductivity range as the water to be sampled.

b. Rinse the conductivity sensor with a small amount of the same standard.

c. Without removing the sonde guard, carefully immerse the probe end of the sonde into the solution. Gently rotate and/or move the sonde up and down to dislodge any air bubbles from the conductivity cell. The probe must be completely immersed past its vent hole.

d. Allow at least one minute for temperature equilibration before proceeding.

e. From the *Calibration Mode* menu, select *Conductivity* and then *SpCond* to access the specific conductivity calibration procedure.

f. Enter the calibration value of the standard being used in **mS/cm** at 25°C and press <*Enter*>. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

g. Observe the readings under Specific Conductivity (*SpC*), Conductivity (*CND*) and Temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>.

h. When the calibration has been accepted, press any key to return to the *Calibration Mode* menu.

i. Rinse the sonde with deionized water and allow to dry.

j. Press <*Esc*> until the *Main* Menu appears. Choose <*Run*>. As a calibration check, repeat steps 2(a) through 2(d) with all 3 calibration standards, rinsing and drying the sonde between changes of calibration solutions. Record the standard concentration and associated reading in the field notebook.

3. pH

When calibrating for pH, the standard pH value must be corrected for temperature. Refer to Table 2 for temperature correction factors.

a. Place approximately 200 mL of pH 7 buffer in a clean calibration cup, and carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

b. From the *Calibration Mode* menu, select *ISE1 pH* to access the pH calibration options. Select *2 point* by pressing <*Enter*> when it is highlighted and input the pH value (7.00) of the buffer at the prompt. Press <*Enter*> and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution.

c. Observe the readings for *pH* and for Temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>.

d. When the display indicates that the calibration is accepted, press any key to continue. The display will show the calibrated reading for the pH 7 buffer.

e. Press <*Enter*> to continue.

f. Rinse the sonde with deionized water and dry.

g. Place approximately 200 mL of a second pH buffer solution in a clean calibration cup. The buffer solutions selected should bracket the anticipated sample pH. Carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

h. Input the value of the second buffer at the prompt. Press <*Enter*> and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution.

i. Observe the readings for *pH* and Temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>.

j. When the display indicates that the second calibration point is accepted, press any key to continue. The display will show the calibrated reading for the second pH buffer.

k. Press <*Esc*> twice to return to the *Main* menu.

l. Rinse the sonde in water and dry the sonde.

m. From the *Main* menu, select <*Run*>.

n. Place approximately 200 mL of the third pH buffer (either 4 or 10) in a clean calibration cup, and carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

o. Observe the *pH* value and record. As a calibration check, repeat this step with <u>all</u> the calibration standards rinsing and drying the sonde between changes of calibration solutions. Record the standard pH value and associated reading in the field notebook.

4. Eh (ORP)

Calibration of the Eh sensor is not required, but a calibration check is recommended.

a. Place approximately 200 mL of Solution A in a clean calibration cup, and carefully immerse the probe end of the sonde into the solution. Allow at least 1 minute for temperature equilibration before proceeding.

b. From the *Calibrate Mode* menu, select *ISE2 Orp* to access the Eh calibration option. Input the Eh value (234) of the buffer at the prompt. Press <*Enter*> and the current values of all enabled sensors will appear on the screen and will change with time as they stabilize in the solution.

c. Observe the readings for Eh *(ORP)* and for Temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>.

d.. When the display indicates that the calibration is accepted, press any key to continue. Record the Eh value for Solution A in the field notebook.

e. Press <*Enter*> again to continue.

f. Rinse the sonde with deionized water and dry.

g. Place approximately 200 mL of Eh solution B in a clean calibration cup. Carefully immerse the probe end of the sonde into the solution.

h.. Press <*Esc*> until the *Main Menu* appears. Select <*Run*>.

i. Observe the readings for Eh (*Orp)* and temperature (*TMP*). When they show no significant change for approximately 30 seconds, press <*Y*>. Record the Eh value for Solution B in the field notebook.

j. Rinse the sonde with deionized water and allow to dry.

E. Sample Analysis

Lower the sampling device into the well and set at the desired depth for purging. If the initial purge water is silty, it is recommended that pumping continue until the discharge water is less silty before in-line measurements are taken. Air in the flow-cell can also affect the readings, especially conductivity and DO. To alleviate air elevate the sonde end of the flow cell to allow any air bubbles to escape. Install the sonde so the conductivity sensor vent is facing upward when the sonde and flow cell are oriented horizontally and ensure that all fittings/connections are tight to eliminate potential for air leaking into the system.

1. Remove suite of probes from flow-through cell. Rinse all probes with deionized water.

2. Connect 3/8" OD Tygon inflow tubing from the pump to the in-port on the flow cell and the other end of the inflow tubing to the pump. Connect the 1/2" OD Tygon discharge tubing to the out-port of the flow cell and place the other end of the outflow tubing in an appropriate container if containerizing purge water is required. Refer to the project work plan for purge water disposal requirements.

3. Power on the instrument and check the display for readings.

4. Start the sampling pump and check for leaks in the discharge lines or flow-through cell. If leaking is observed, stop the pump and repair the leak. Record the initial meter readings.

5. Examine the flow-through cell and determine whether discharge water is entering and exiting the cell properly. Once the air is purged from the pump and discharge hoses, the flow-through cell should be completely filled with water and a steady flow of water should be exiting the outflow line from the cell.

6. Continue to pump until the readings stabilize. Record each value on the appropriate field form, including the units displayed for each parameter. Collect the required groundwater samples

7. When sample collection is complete, stop the pump and disconnect inflow discharge hose. Remove the suite of probes from the flow-through cell and rinse the probes, flow-through cell, and inflow and outflow lines with deionized water.

8. Attach storage boot to pH probe.

Sample measurement can also be performed in the calibration cup.

1. Screw the calibration cup onto the multiprobe and fill half-full with deionized water.

2. Place the cap on the top of the cup and shake the multiprobe to rinse.

3. With the sensors pointing up, remove the cap and discard the wash water. Rinse the sensors twice with a small volume of the sample to be measured. Discard the rinse.

4. Fill the cup with the sample to be measured so that the multiprobe is completely immersed.

5. Allow 1 - 3 minutes for the readings to stabilize and record.

6. Repeat Steps 3 - 5 for each sample to be measured.

F. Electrode Storage

1. Dissolved Oxygen Probe

   a. Short Term: Store installed in sonde in flow cell with ¼" - ½" of deionized water in the flow cell for moisture. DO NOT store directly in water.

b. Long Term: Store in water with membrane in place. The membrane and KCl solution must be replaced prior to use.

2. Temperature/Conductivity Probe

a. Short Term: No special storage requirements. Can be stored wet or dry.

b. Long Term: No special storage requirements. Clean thoroughly prior to storage.

3. pH/Eh Probe

a. Short Term: Can be stored installed in sonde in flow cell with ¼" - ½" of H_2O in flow cell for moisture for up to one week.

b. Long Term: Store the probe in 2M KCl solution in the pH/ORP storage bottle. The vacant port on the sonde must be plugged.

G. Electrode Maintenance

1. Dissolved Oxygen Probe

Refer to maintenance procedure provided in the instruction manual if the DO charge is <25 mV or >75 mV and for membrance replacement.

2. Temperature/Conductivity Probe

Clean thermistor and conductivity electrodes with soft brush and deionized water. A mild detergent may be used for cleaning, if required.

3. pH/Eh Probe

a. Clean with deionized water as necessary.

b. If rehydration of the electrode junction is required, soak the probe in 2M KCl solution for eight hours.

Table 1 - Barometric Pressures

Elevation (feet)	Elevation (meters)	Barometric Pressure (millibars)	Barometric Pressure (mm of Hg)
400	122	996	747
450	137	994	745
500	152	991	744
550	168	989	742
600	183	987	740
650	198	985	739
700	213	983	737
750	229	981	735
800	244	979	734
850	259	976	732
900	274	974	731
950	290	972	729
1,000	305	970	728
1,050	320	968	726
1,100	335	966	724
1,150	351	964	723
1,200	366	962	721
1,250	381	960	720
1,300	396	957	718
1,350	412	955	717
1,400	427	953	715
1,450	442	951	713
1,500	457	949	712
1,550	473	947	710
1,600	488	945	709
1,650	503	943	707
1,700	518	941	706
1,750	534	939	704
1,800	549	937	703

Table 2 • Temperature Correction for pH Buffer Solutions

	pH 4.01 ± .01@25°C Red Potassium Hydrogen Phthalate Buffer, 0.05 Molar	pH 7.00 ± .01@25°C Yellow Sodium and Potassium Phosphate Buffer, 0.05 Molar	pH 10.01 ± .01@25°C Blue Sodium Carbonate Buffer, 0.025 Molar
°C	Calculated pH	Calculated pH	Calculated pH
0	4.00	7.12	10.32
5	4.00	--	10.25
10	4.00	7.06	10.18
15	4.00	--	10.12
20	4.00	7.02	10.06
25	4.00	7.00	10.01
30	4.01	6.99	9.97
35	4.02	6.98	9.93
40	4.03	6.97	9.89
45	4.04	--	9.86
50	4.06	--	9.83
60	4.09	6.98	--
70	4.13	--	--
80	4.16	7.04	--
90	4.19	7.09	--

FTC&H **STANDARD OPERATING PROCEDURE** **SOP 14-10**
Methanol Preservation Method for Volatile Organic Compounds in Soil
07/07/1998; Revised 07/07/1998

Scope: This soil sampling method is designed to minimize the loss of volatile organic compounds (VOC) due to sample handling and biodegradation during collection, shipment, and storage. Using a syringe barrel, a core sample is obtained and transferred to a glass vial. A known volume of methanol is then added to the sample, acting as both a preservative and extraction solvent. A second bulk sample is also collected for determination of percent total solids.

Equipment: Top-loading balance (±0.1 grams [g])
Small brush
5, 10, 20 g weights
Knife
Plastic syringes, 30 cc
Sample bottles (2 oz glass jars with Teflon®-lined screw caps)
Methanol (25 mL ampules, purge and trap grade)

References: Lewis, T.E., Crockett, A.B., Siegrist, R.L., and Zarrabi, K., *Soil Sampling and Analysis for Volatile Organic Compounds*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, February 1991.

Michigan Department of Environmental Quality, *Environmental Response Division Guidance Memo, New VOC Sediment Sampling Method 5035, ERD Field Sampling Procedure*, March 31, 1998.

Michigan Department of Environmental Quality Environmental Laboratory, *Soil Sample Collection and Methanol Preservation for Volatile Analysis*, March 26, 1998.

U.S. Environmental Protection Agency, *Method 5035*, Revision 0, December 1996.

Procedure:

1. Place balance on a clean, level surface and turn the power on. The sample pan should be free of debris. If needed, clean pan lightly with a brush.

2. Zero the balance. As a check of system accuracy, place a 5 gram standard weight on the pan and wait for a stable reading. If the balance does not read 5 g ± 0.1 g, refer to the balance operation manual for corrective action.

3. Place a clean, capped 2 oz. amber sample jar on the balance and tare the jar weight.

4. Prepare a sample syringe for sample collection by cutting of the end of the syringe near the zero cc mark.

5. Insert the syringe barrel to the 20 cc mark into the soil to be sampled.

6. Pushing the syringe plunger, quickly transfer the soil sample into the tared jar, cap, and wiegh. Record the sample weight. The sample weight must be 25g ± 1 g or a new sample must be obtained.

7. Once the sample weight has been recorded, empty the contents of a 25 mL methanol ampule into the sample jar and cap tightly. Invert several times to mix.

   Note: It is critical that all of the methanol be transferred to the sample jar. If any methanol is lost during transfer, a new sample must be prepared.

8. Appropriately label the sample, including the sample weight and volume of methanol used. Place the sample in a ziplock bag and store on ice or at 4°C until delivered to the laboratory. Sample hold time is 14 days.

9. Fill a second 2 oz jar with the same soil and label. This bulk sample will be used by the laboratory to determine the percent total solids of the soil.

10. Record the sample time and ID on the chain-of-custody in accordance with SOP 3-2.

Quality Control

1. A field blank must be prepared for every batch of samples collected during a day. The field blank consists of 25 mL of methanol transferred to a clean sample collection jar. The transfer should be made at/near the time of sample collection and the blank should be exposed to the same sampling environment as the samples.

2. Refer to the project work plan to determine if additional QC samples are required.

3. Duplicate samples should be prepared for critical projects or when resampling will not be an option.

STANDARD OPERATING PROCEDURE **SOP 18-04**
Water Level Measurement - Electric Tape Method
11/20/1996; Revised 02/15/00

Scope: This SOP describes water level measurement using an electric tape.

Equipment: Water level meter, QED Sample Pro Model 6000 or Solinst Model 101
Clean paper toweling
Spray bottle of Liquinox® soap solution
Spray bottle of deionized, organic-free rinse water
Field notebook

Procedure:

A. Calibration Procedure (Electric Tape to Wet Tape)

Prior to each monitoring event, verify the accuracy of the electric tape by measuring the depth to water at one monitoring well using the both the electric tape and wet-tape method (SOP 18-03). If depth to water varies significantly across the site, choose two monitoring wells (at a minimum) with the greatest difference in depth to water and compare wet tape and electric tape measurements from each well. If the readings differ, a correction factor for the electric tape reading is required. The correction factor is simply the difference , in 0.01 ft., between the electric tape measurement and the wet-tape measurement.

B. Water Level Measurement

1. Verify the well location and record in the field notes. Remove the lock and uncap the well carefully to avoid introducing foreign material into the well.

2. Decontaminate the electric tape and probe with the soap solution and rinse with organic-free, deionized water prior to each water level measurement.

3. Using the test button, verify that the audio response and the visual indicator are both operating.

4. Lower the probe into the well slowly until the audio or visual response is activated. Raise and lower the probe several times to obtain an accurate measurement.

5. Mark the point on the tape at the well reference point with finger. Record the depth to water measurement (to the nearest 0.01 foot) and the reference point. The depth to water should be referenced to the measuring point marked at the top of the innermost well casing. Where a measuring point has not been marked at the top of casing, the measuring point should be assumed to be at the top of the innermost casing on the north side of the casing.

6. Retrieve the tape and probe and decontaminate with the soap solution followed by a deionized water rinse.

7. Recap and lock the well.

8. Calculate the groundwater elevation using the following equation:

   Water elevation, ft-msl = (Reference elevation) - (Depth to water ± Correction factor)

STATIC WATER LEVEL DOCUMENTATION

Project Name: _____ Method: _____ Wet Tape _____ Electric Tape

Project No.: _____ Recorded by: _____

Project Location: _____ Date: _____

Well No.	Time	Reference Elevation	Wet Tape Method			Electric Tape Method		Water Elevation (ft-msl)	Notes
			Hold Value	Read Value	SWL (HV-RV)	Depth to Water	Correction Factor		

KAR LABORATORIES, INC.

CHAIN-OF-CUSTODY PROTOCOL

STANDARD OPERATING PROCEDURE

Sample Receipt, Handling and Storage (Chain-of-Custody)

Principal References : *Quality Assurance Manual*, KAR Laboratories, Inc.; *Standard Methods*, 18th Ed., Section 1060.

Application : This SOP applies to all samples collected, received, handled or controlled by KAR personnel.

Summary of Method : Containers are shipped in appropriate packaging to the client with a chain-of-custody form and any required QC blanks. Once collected, the sample is shipped or delivered to the laboratory, where it is received by a member of the Client Services staff. The relinquishing and receiving parties both sign the chain-of-custody form after all available relevant project and sample information is obtained. The sample is logged into the LIMS system, filtered and/or preserved if necessary, and delivered to the appropriate lab sample storage area. After login peer-review, all paperwork is placed in the active project files. Following lab analysis, the sample is stored for a period of time before disposal.

Discussion : The procedures and considerations outlined below will ensure that KAR personnel maintain the integrity of all samples placed under KAR's control for valid laboratory analysis. This SOP contains essential actions which must be followed in order for clients to receive accurate and valid analytical results.

A sample is considered to be under the laboratory's custody when 1) it has been received into physical possession, 2) is in ready view after receipt, 3) is secured to prevent tampering, and/or 4) has been placed in a secure area restricted to authorized personnel. The primary goal of chain-of-custody procedures is to maintain the identity and integrity of a sample from collection to analysis.

Apparatus & Equipment :

Containers, free of the analyte(s) of interest
Labels
Chain-of-custody form
Chain-of-custody seals
Shippers and packaging accessories
Ice packs
Waterproof pens

Safety :

1. All samples should be handled and regarded as potentially hazardous. All lab personnel should wear safety glasses, labcoat and protective gloves when handling samples.

2. The various acids and chemicals used to preserve samples are generally either corrosive or toxic. Perform all sample preservation in a fume hood wearing safety glasses, labcoat and gloves.

Procedures : Shipping Containers

1. Determine the number of samples and parameters requested by the client from the quotation on file or a memo from contact with the client.
2. Following the Container, Volume, Preservation and Holding Time table (Table 1), assemble the containers needed for the required analyses.
3. Using the appropriate packaging, secure the sample containers in a shipper or cooler (styrofoam shipper or cooler) with a sufficient number of cold/ice packs for return delivery of samples that must be kept at or near 4°C. Include a temperature blank for all "Level 4 QA" projects. Include properly prepared trip blanks and materials for field blanks if required.
4. Include sampling instructions or special considerations for holding times and/or preservation in the field if necessary.
5. Include labels and a chain-of-custody form(Attachment 2) with all container shipments.
6. Document all containers being shipped for the specific client and project and place in the client file.
7. Secure the packaging, sealing the shipping container with custody seal labels if necessary, and send to the client as requested.

Sample Receipt

1. All samples delivered to KAR for analysis will be directed to the Client Services sample receiving area.
2. Many samples arrive via a delivery person without a chain-of-custody document prepared by the sample collection personnel. In these cases, a KAR chain-of-custody (Attachment 2) must be filled out in waterproof ink completely and accurately and signed both by the person delivering the sample and the KAR employee receiving the sample.
3. Samples associated with "Level 4 QA" projects will have a temperature blank in the cooler, alongside the samples. The temperature of this blank must be measured and recorded immediately upon opening the cooler by using a calibrated, certified mercury thermometer. If the temperature is below 1°Celsius or above 6°Celsius (or outside of project/client specifications), this must be noted and the project manager must be contacted immediately.
4. All of the following information must be recorded on the KAR chain-of-custody (Attachment 2):
   - Client name
   - Client address
   - Client phone number and fax number
   - Client representative to whom report should be sent
   - Turnaround time
   - Client Project ID (if supplied)
   - Whether the sample was collected by the Client or KAR
   - Sample ID supplied by client
   - Date each sample was collected
   - Time each sample was collected
   - Sample type (matrix)
   - Container type
   - Container size
   - Number of containers of each size and type

- Analyses requested on each sample
- Whether the sample is associated with a waste characterization
- Whether the sample will require Part 201 detection limits
- Special analytical or reporting instructions from the client
- Signature of the person relinquishing the sample
- Signature of the person receiving the sample
- Date and time that sample custody was transferred

5. Clients delivering samples using their own chain-of-custody form must still provide all the information outlined above.
6. Samples and chain-of-custody records arriving by common carrier are removed from the shipping container (shipper or cooler) and inspected for all the information outlined above.
7. Every sample arriving at KAR must be thoroughly inspected for the following possible problems:
   - lack of container integrity
   - improper container for the requested parameters
   - improper collection of the sample
   - insufficient sample amount
   - improper labeling
   - improper preservation
   - any disagreement between the label and the chain-of-custody document
   - any "near holding time" situations
   - any "past holding time" violations
   - any potentially hazardous properties to which analysts must be alerted
8. Document all problems involving labeling or chain-of-custody discrepancies on the KAR chain-of-custody form (Attachment 2).
9. All problems, errors and discepancies must be relayed to a Project Manager and/or the client and resolved as soon as possible after sample receipt. Note any condition codes that must be applied to specif c parameters during sample login. Standard holding times and required preservation are outlined in the Container, Volume, Preservation and Holding Times document (Table 1). All available LIMS condition codes for qualifying incoming samples are found in the LIMS Condition Codes document (Table 3).
10. Notify analysts and/or their supervisors immediately of any samples by bringing special circumstances to their attention as soon as possible after sample receipt. This is especially true for "near holding time" situations and any special requests from the client.

    NOTE: A sample arriving on a standard turnaround basis but requiring expedited preparation or analysis to meet holding times must be treated like an expedited request. Lab managers should be notified of the need using the Rush Notification Form (Attachment 4) or via the e-mail rush approval process, and the client must be notified that expedited service charges will be added to the invoice.

11. Note any potential hazards to the safety of analysts or the integrity of sensitive instrumentation. These samples must be clearly marked with all known hazards and a memo to the analyst posted in the internal comments field during sample login. Alert analysts also to samples that are known to be highly contaminated in order to prevent instrument contamination.
12. Filter, composite and/or preserve all samples requiring such treatment in the Login Prep lab adjacent to Sample Receiving. All preservation must be done in the fume hood with the appropriate safety protection being worn. Following preservation, each sample (except VOCs) must be checked for proper pH adjustment. A pH strip with a range of 0-6 S.U. will be used to check pH of acid preserved samples. A pH strip with a range of 7.5-14 S.U. will be used to check pH of base preserved samples.

13. Proper preservation will also be confirmed by the client services department for all samples preserved by clients. For "Level 4 QA" samples only: If the sample requires additional preservative, the technician will note on the chain-of-custody the original pH, amount of preservative added, and the final pH of sample.

Project Login

1. Please refer to KAR SOP KG030, "New Project Login", for complete discussion.
2. Once all essential information has been obtained, the samples must be logged into the LIMS database. In many cases, a project will be activated and samples logged in before all sample receipt discrepancies have been resolved. In these cases, Project Managers must make every reasonable effort to contact the client and resolve problems as soon as possible. Document all efforts to contact clients along with all corrective actions taken.
3. Place all samples that are "on-hold" (while project/sample information discrepancies are resolved) in a secure, appropriate sample storage area.
4. All samples must be assigned its own unique KAR sample number and labeled properly during the login process. Print labels from LIMS during login. All labels must include the KAR identification, Client name, Client identification, the time collected and any preservative added.
5. With every sample being labeled, verify that the KAR label matches the Client identification.
6. Assemble all hardcopy documents for each project and submit to a Project Manager for login peer-review. Following any necessary corrective actions, place project documents in the active projects file in numerical order according to KAR project number.

Sample Handling (Client Services Staff)

1. All samples must be logged in and prepared for delivery to the laboratories as soon as possible after receipt. The Client Services staff must ensure that the following errors are prevented:
   - mislabeling of samples
   - breakage of containers or spillage of their contents
   - cross-contamination of samples through air (volatiles), filtering (metals, WQ), etc.
   - improper chemical preservation
   - failure to maintain samples at the proper temperature
   - violation of holding times
   - sample tampering by outside agents
2. The Client Services staff is solely responsible for the proper handling, storage, preservation and labeling of all samples until they are delivered to their proper place in each laboratory area. Separate all samples and paperwork from other projects arriving concurrently.
3. Deliver all prepared samples to one of the following lab sample storage areas:
   - Walk-in cooler
   - Login Prep Lab, hazardous waste refrigerator
   - Water Quality I bench area
   - Volatiles Lab refrigerator
   - Semi-volatiles Prep Lab refrigerator
   - Trace Metals Prep Lab bench area
   - Microbiology Lab sample refrigerator
   - Login Prep Lab "On-hold" refrigerators (2)

Sample Handling (Laboratory Staff)

1. Once delivered, all laboratory staff are then solely responsible for the proper handling, storage and disposal of samples throughout the analytical process and until the client receives the final report.
2. Accurate, defensible results must be obtained within regulatory holding times. Perform all analyses according to established methods and SOPs within the regulatory holding times. Report all holding time failures to the Laboratory Supervisor.
3. All necessary conditions of preservation must be maintained to ensure sample integrity. Samples removed from refrigerated storage must be returned as soon as possible after subsampling for analysis.
4. The removal of subsamples from a common container must be performed with extreme care; not only to prevent contamination but also to maintain the representative nature of the sample.
5. Handle the sample carefully and perform analyses efficiently to prevent losses through carelessness or poor planning and so that all requested analyses can be performed.
6. Bring all accidents or oversights that either compromise the sample or prevent all requested analyses from being performed to the attention of the Laboratory Supervisor immediately. All errors which compromise a sample's integrity must be brought to the client's attention as soon as possible by a Project Manager. In addition to any analytical considerations that may affect data validity, analysts must qualify all results that may be in doubt due to improper handling of the sample.
7. The peer-review or data validation process may discover an inconsistency that must be investigated. A client may also want a sample reanalyzed if an unexpected result was reported. Maintain the integrity of all samples in storage until they are past holding time.

Sample Disposal

1. All samples should be stored for at least 14 days in the event that KAR is asked to verify labeling or analytical results. For long-term storage, all samples should be placed in the Sample Storage area in the designated locations. The actual disposal of samples is covered by the Waste Management Plan, which is administered by the Waste Manager.
2. All samples requiring Level 4 analysis and QC traceability must be saved under refrigerated conditions for a minimum of 60 days from the date the final project report is issued. Requests for longer periods of storage will be considered on a case-by-case basis.

TABLE 1

CONTAINERS, VOLUMES, PRESERVATION AND HOLDING TIMES

Determination	Container	Minimum Sample Size *mL*	Preservation	Maximum Storage Recommended/ Regulatory†
Acidity	P, G(B)	100	Refrigerate	24 h/14 d
Alkalinity	P, G	200	Refrigerate	24 h/14 d
BOD	P, G	1000	Refrigerate	6 h/48 h
Boron	P	100	None required	28 d/6 months
Bromide	P, G	—	None required	28 d/28 d
Carbon, organic, total	G	100	Analyze immediately; or refrigerate and add HCl to pH<2	7 d/28 d
Carbon dioxide	P, G	100	Analyze immediately	stat/N.S.
COD	P, G	100	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7 d/28 d
Chlorine, residual	P, G	500	Analyze immediately	0.5 h/stat
Chlorine dioxide	P, G	500	Analyze immediately	0.5 h/N.S.
Chlorophyll	P, G	500	30 d in dark	30 d/N.S.
Color	P, G	500	Refrigerate	48 h/48 h
Conductivity	P, G	500	Refrigerate	28 d/28 d
Cyanide:				
Total	P, G	500	Add NaOH to pH>12, refrigerate in dark	24 h/14 d; 24 h if sulfide present
Amenable to chlorination	P, G	500	Add 100 mg $Na_2S_2O_3$/L	stat/14 d; 24 h if sulfide present
Fluoride	P	300	None required	28 d/28 d
Hardness	P, G	100	Add HNO_3 to pH<2	6 months/6 months
Iodine	P, G	500	Analyze immediately	0.5 h/N.S.
Metals, general	P(A), G(A)	—	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months/6 months
Chromium VI	P(A), G(A)	300	Refrigerate	24 h/24 h
Copper by colorimetry*				
Mercury	P(A), G(A)	500	Add HNO_3 to pH<2, 4°C, refrigerate	28 d/28 d
Nitrogen:				
Ammonia	P, G	500	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d/28 d
Nitrate	P, G	100	Analyze as soon as possible or refrigerate	48 h/48 h (28 d for chlorinated samples)
Nitrate + nitrite	P, G	200	Add H_2SO_4 to pH<2, refrigerate	none/28 d
Nitrite	P, G	100	Analyze as soon as possible or refrigerate	none/48 h
Organic, Kjeldahl	P, G	500	Refrigerate; add H_2SO_4 to pH<2	7 d/28 d
Odor	G	500	Analyze as soon as possible; refrigerate	6 h/N.S.
Oil and grease	G, wide-mouth calibrated	1000	Add H_2SO_4 to pH<2, refrigerate	28 d/28 d
Organic compounds:				
Pesticides	G(S), TFE-lined cap	—	Refrigerate; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/7 d until extraction; 40 d after extraction
Phenols	P, G	500	Refrigerate, add H_2SO_4 to pH<2	*/28 d
Purgeables by purge and trap	G, TFE-lined cap	50	Refrigerate; add HCl to pH > 2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/14 d
Oxygen, dissolved:	G, BOD bottle	300		
Electrode			Analyze immediately	0.5 h/stat
Winkler			Titration may be delayed after acidification	8 h/8 h
Ozone	G	1000	Analyze immediately	0.5 h/N.S.
pH	P, G	—	Analyze immediately	2 h/stat
Phosphate	G(A)	100	For dissolved phosphate filter immediately; refrigerate	48 h/N.S.
Salinity	G, wax seal	240	Analyze immediately or use wax seal	6 months/N.S.
Silica	P	—	Refrigerate, do not freeze	28 d/28 d
Sludge digester gas	G, gas bottle	—	—	N.S.
Solids	P, G	—	Refrigerate	7 d/2–7 d; see cited reference
Sulfate	P, G	—	Refrigerate	28 d/28 d
Sulfide	P, G	100	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH>9	28 d/7 d
Taste	G	500	Analyze as soon as possible; refrigerate	24 h/N.S.
Temperature	P, G	—	Analyze immediately	stat/stat
Turbidity	P, G	—	Analyze same day; store in dark up to 24 h, refrigerate	24 h/48 h

KAR Laboratories, Inc. (616-381-9666) www.karlabs.com (Client please complete shaded areas)

Client:

Attn:

Phone: ( ) Fax: ( )

Project Name:

Project #

P.O. #

Sampled by: ☐ KAR ☐ Client Initials __ __ __

Turnaround Time:
- ☐ 10-business days
- ☐ 5-business days (x 1.5)
- ☐ 3-business days (x 2.0)
- ☐ Emergency (quote)
- ☐ Monthly

Waste characterization: Yes No
Part 201: Yes No
Part 213: Yes No

Requested Analyses

KAR use only
Proj#: ______
Login: ______
Date: ______
c-of-c Y N
labels Y N
LODs Y N
contain Y N
headspace Y N
amount Y N
hold time Y N
rush cost Y N
preservation Y N
intact Y N

#	Sample Identification	Sample Info: Date	Time	Matrix	Sample Containers: Type	Size	#									Remarks

Relinquished By:	Received By:	Date/Time:	Notes:
Relinquished By:	Received By:	Date/Time:	

TABLE 3

LIMS CONDITION CODES

CODE	REPORT COMMENT
AC	Analysis was canceled by client prior to completion.
AL	Analysis canceled due to Laboratory error.
AZ	Analysis cannot be performed on this sample type.
CI	Client indicated that sample contained residual chlorine.
CO	Definition of Corrosivity does not apply.
CR	Chlorine residual in sample
CU	Client unable to collect sample.
DA	Sample container broken; data is approximate
DW	Analysis canceled-well dry at time of collection
FR	Sample site flooded; refer to Storm Drain.
HS	Headspace due to elevated sample temp; result is approx.
IS	Insufficient sample to achieve requested detection limit.
MC	Measurement was not performed by KAR Labs.
NF	No flow in wastestream - analysis canceled
NS	No sample at pick up - autosampler malfunction.
OH	Analysis placed on hold by client
PF	Analysis should be performed in field; result is approx.
SA	Sample was lost due to Laboratory accident
SB	Sample bottle was received broken
SC	Improper sample container; result is approximate.
SE	Sample extracted by client
SF	Sample received frozen; result is approximate
ST	Improper sample collection; result is approximate.
SI	Improper sample collection; analysis canceled.
SM	Sampling media may be inappropriate for this compound.
SP	Improper sample preservation; result is approximate.
SQ	Insufficient sample amount to perform the analysis.
SR	Sample received past holding time; result is approximate.
SS	Analysis ordered past holding time; result is approximate.
SU	Sample received in unusual container
US	Unable to collect sample-analysis canceled.

ATTACHMENT 4

****

RUSH ANALYSIS REQUEST FORM

Client: Phone: FAX:

Contact:

Parameter(s):

Sample type(s): # of Samples:

Sample arrival date:

Requested TA:

Special instructions/LODs:

CS Tech: Date: Time:

OK'd by: Date: Time:

****

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: Garrett J. Ervin Date: 10/12/00
Garrett Ervin

Supervisor: Michael Jaeger Date: 10/12/00
Michael Jaeger

Laboratory Director: Michael Jaeger Date: 10/12/00
Michael Jaeger

QA Approval: Pollyann Nee Date: 12 Oct-2000
Pollyann Nee

KAR LABORATORIES, INC.

ANALYTICAL METHODS

KAR Method: **KM6020**
Revision 0 9/29/97
Revision 1.1 5/18/97
Revision 2.1 6/04/98

STANDARD OPERATING PROCEDURE

EPA METHOD 6020

Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma-Mass Spectroscopy

1. Principal References

1.1 RCRA SW-846 Revision 0, September 1994.
HP 4500 ChemStation Operator's Manual Revision 3.3, April 1996.

2. Scope and Application

2.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-ppb (µg/L) concentrations of a large number of elements in water samples and in waste extracts or digestates. When measurement of dissolved constituents is required, samples generally must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

2.2 ICP-MS has been applied to the determination of more than 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices and operating conditions.

2.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interference and take appropriate action to ensure data of known quality.

2.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

Element		Chemical Abstracts Services registry Number (CASRN)
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Lead	Pb	7439-92-1
Manganese	Mn	7439-96-5
Nickel	Ni	7440-02-0
Silver	Ag	7440-22-4
Thallium	Tl	7440-28-0
Zinc	Zn	7440-66-6

Table 1: This method is applicable to the above listed elements. Additional elements may be determined pending demonstration of accuracy and precision in the waste being analyzed.

3. Summary of Method

3.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods.

3.2 This SOP describes the multi-element determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled argon plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation of background ions contributed by the plasma gas, reagents and

constituents of the sample matrix.

4. **Interferences**

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). The HP-4500 ChemStation data system is used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences which could affect ICP-MS determinations have been identified. Examples include $ArCl^+$ ions on the As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotopes abundances from the literature, the most precise coefficients for an instrument must be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction of arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal): corrected arsenic signal (using natural isotopes abundances for coefficient approximations)=

(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z).

Note: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes or ^{82}Kr from krypton contamination in the Ar). Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations)=

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

(Where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

Note: Cadmium values will be biased low by this type of equation, $^{92}ZrO^+$ ions contribute at mz 108, but use of m/z 111 for Cd is even subject to direct ($^{92}ZrOH^+$) ions and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

4.2 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and

transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solids levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1 + 4) or greater dilution has been performed.

4.3 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

5. Apparatus and Equipment

5.1 Hewlett-Packard HP 4500 ICP-MS system which is capable of providing resolution better than or equal to unit resolution at 10% peak height. The HP 4500 mass range of 2-260 AMU exceeds the method requirement of 2-240 AMU. The HP 4500 ChemStation allows automatic corrections for isobaric interferences and correction for internal standard responses as required by the method. All critical argon flows including nebulizer argon are under mass flow controller control and a peristaltic pump is used for sample introduction.

5.1.1 Includes HP 4500 ICP-MS Instrument, ChemStation, HP LaserJet printer and Cetac ASX-500 Autosampler.

5.1.2 Consumable parts:

Part Number	Description
G1820-65215	Peri-Pump Tubing (Tygon)
G1820-65216	Peri-Pump Tubing (ISAMAPRENE)
G1820-65219	Peri-Pump Tubing (Kit for On-line ISTD)
G1820-65220	Peri-Pump Tubing (ISTD)
G1820-65104	Tygon Tubing (500 mm)
G1820-65106	Y Connectors
G1820-65221	Drain Tubing Kit
G1820-65036	Babington Nebulizer Assembly

5063-5261	Babington Nebulizer
G1820-65199	O-Rings (for Babington Neb.)
5063-5262	Adapter for Babington Nebulizer (Cap Assembly)
G1820-65198	O-Rings (for Caps)
G1820-65009	3 Meter Teflon Tube (Sample)
G1820-80234	Spray Chamber (Pyrex)
G1820-80236	Spray Chamber (Quartz)
G1820-65028	Torch (Quartz)
G1820-65061	Work Coil
G1820-65206	Sample Cone (Nickel)
G1820-65025	O-Ring for Sampling Cone
G1820-65212	Skimmer Cone (Nickel)
G1820-65243	Electron Multiplier

Table 2: HP 4500 Consumable Parts and supplies

5.2 15 mL polypropylene test tubes for samples (Fisher Scientific #14-956-7E) and 50 mL polypropylene centrifuge tubes for standards (Fisher Scientific part #14-375-150).

5.3 Calibrated mechanical pipetters in the following rangers
- 10-100 µL
- 100-1000 µL
- 1000-5000 µL

5.4 Trace metal grade pipette tips.

5.5 Talc-free gloves.

5.6 Argon gas supply (high purity grade gas or liquid, 99.99%).

6. Preventative Maintenance

6.1 KAR Laboratories, Inc. has a full service contract on the HP4500 ICP-MS.

6.2 Record all maintenance in the HP 4500 ICP-MS maintenance logbook.

6.3 Each day check the following:

1. Argon supply - replace when needed.

2. Waste container - empty when needed.
3. The autosampler rinse and optional rinse container - change solution (2% HNO_3) daily.
4. Vacuum oil - fill if needed and change every six months.
5. Sample pump tubing - replace after every 24 hours of use or when needed.

6.4 The following should be cleaned or replaced when tuning becomes more difficult:

1. Sampler and skimmer cones
2. Nebulizer
3. Spray chamber
4. Extraction lenses

6.5 Refer to the HP 4500 ChemStation Administration and Maintenance Manual (revision 3.3, April 1996) when other problems arise.

7. Safety

7.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices should be practiced at all times.

7.2 Safety glasses and acid-resistant gloves should be worn at all times when handling samples or reagents, or when in the vicinity of others handling these items.

7.3 Liquid argon represents a potential cryogenic and suffocation hazard and safe handling procedures should be employed at all times when handling liquid argon tanks and fittings.

7.4 The HP 4500 is fully interlocked to prevent user exposure to harmful electrical voltages, radio frequency emissions, ultraviolet radiation, high temperatures and other hazards. At no time should the operator attempt to disable these interlocks or operate the instrument if any safety interlock is suspected to be disabled.

7.5 Spilled samples and reagents should be cleaned up from instrument and laboratory surfaces immediately. Acid spills should be neutralized with sodium bicarbonate solution before cleanup.

7.6 All additional company safety practices and procedures should be followed at all times.

8. Standards and Reagents

8.1 Multi-element stock solutions and single-element stock solutions are purchased from a commercial supplier (Spex). Each standard comes with a certificate of analysis and expires in one year. Fresh mixed standards from the Spex stock standards should be prepared as needed, with the realization the concentration can change on aging. Solutions made from stock standard have a shelf life of 6 months.

8.2 Nitric Acid, concentrated "Trace Metal" Fisher Scientific 2.5L in glass, catalog #A509-212.

8.3 Hydrochloric Acid, concentrated "Trace Metal" Fisher Scientific 2.5L in glass, catalog #A508-212.

8.4 Reagent water equivalent to ASTM Type 1 (ASTM D 1193) >18 Megohm/centimeter resistivity.

8.5 1:1 (vol/vol) nitric acid

8.5.1 Prepare by adding 50 mL concentrated nitric acid to 50 mL ASTM Type 1 water in a clean 125 mL HDPE bottle.

8.6 1:50 (vol/vol) nitric acid

8.6.1 Prepare by adding 2 mL concentrated nitric acid to 98 mL ASTM Type 1 water in a clean 125 mL HDPE bottle.

8.7 HP Tuning solution stock: 1.0mg/L Li, Ce, Y, Tl, in 1% HNO_3.

8.7.1 Prepare by adding in a 100 mL volumetric flask 100 µL of each 1000 mg/L single element stock standard and 1.0 mL of HNO_3 and bring up to volume.

8.8 HP Tuning Solution: 10 µg/L Li, Ce, Y, Tl in 1% HNO_3.

8.8.1 Prepare by adding in a 1000 mL volumetric flask 10.0 mL of HP Tuning Solution stock and 10.0 mL of HNO_3 and bring up to volume.

8.9 Tune Check Solution stock: 100 mg/L Li, Co, In, Tl

8.9.1 Prepare by pipetting 500 µL of each 10,000 mg/L single element stock solution into a 50 mL centrifuge tube. Add 1 mL of 1:1 nitric acid and dilute to 50 mL with reagent water.

8.10 Tune Check Solution: 100 µg/L Li, Co, In, Tl

8.10.1 Prepare by pipetting 50 µL of Tune Check Stock solution into a 50 mL centrifuge tube, add 2 mL 1:1 nitric acid and bring to 50 mL total volume.

8.11 Internal Standard Stock Solution: 10 mg/L ^{6}Li, Sc, Y, In, and Bi.

8.11.1 (Spex cat. # CL-ISS-1).

8.12 Internal Standard Working Solution for on-line addition of internal standards, 1mg/L ^{6}Li, Sc, Y, In, and Bi.

8.12.1 Prepare by pipetting 5mL of Internal Standard Stock into a 50 mL centrifuge tube. Add 2 mL 1:1 nitric acid and bring to 50 mL total volume.

8.13 Calibration standards, certified, purchased from Spex:

8.13.1 Instrument Calibration Standard 1 (Spex cat. #CL-CAL-1). 20 ppm of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn (*Use for calibration standards according to Table 3).*

8.13.2 Instrument Check Standard 1 (Spex cat. #CL-ICS-1). 10 ppm of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn. *(Use for ICV according to Table 4).*

8.13.3 Instrument Check Standard 3 (Spex cat. #CL-ICS-3). 200ppm of Ca, Fe, Mg, K, Na. *(Optional mineral elements.)*

Calibration Level	1	2	3	4
Conc. Trace elements (ppb)	0	10	100	200
Conc. Major elements (ppb)	0	100	1 ppm	10 ppm
Vol. Inst., Cal. Std. 1 (Trace metals, 20 ppm stock)	0	25 uL	250 uL	500 uL
Vol. Inst. Check 3 (major elements, 200 ppm stock)	0	25 uL	250 uL	2.5 mL
Vol. Of 1:1 (vol./vol.) nitric acid	2.0 mL	2.0 mL	2.0 mL	2.0 mL
Final Volume	50 mL	50 mL	50 mL	50 mL

Table 3: Preparation of calibration standard solutions from Spex multi-element calibration mixes.

8.14 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in the calibration curve. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

8.14.1 The calibration blank consists of the same concentrations of the same acid(s) used to prepare the final dilution of the analyte calibration solutions (2 percent HNO_3, (v/v) in reagent water).

8.14.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

8.14.3 The rinse blank consists of 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. This solution needs to be made weekly and change daily.

8.15 Quality Control Standard or Initial Calibration Verification (ICV):

Trace element conc.	50 ppb	250 µL spex Inst. Check 1 (10 ppm Stock)
Major element conc. (Cs, Fe, K, Mg, Na)	500 ppb	125 µL spex Inst. Check 3
Volume of HNO_3	2% HNO_3	2.0 mL of 1:1 (vol.vol.) nitric acid.
Final volume	50 mL	

Table 4: Quality Control Standard (ICV) preparation from Spex prepared stock solutions.

8.16 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl\ ^{16}O$ on ^{51}V and $^{40}Ar^{35}Cl$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolutions of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various polyatomic isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system to within quality control limits.

8.16.1 ICS-A: Dilute Interferents A, (Spex cat. #CL-INT-A2) 1 to 10 by adding 5 mL to a 50 mL plastic centrifuge tube, add 1 mL HNO_3 and bring to 50 mL.

500 mg/L Al, Ca, Mg
200 mg/L Fe

8.16.2 ICS-AB Dilute Analytes B, (Spex cat. #CL-INT-B2) 1 to 500 by adding 100µL to a 50 mL plastic centrifuge tube containing 1 mL HNO_3 and 5 mL Interferents A stock solution. Bring up to 50 mL.

200 µg/L Cd, Ni, Zn
120 µg/L Sb
100 µg/L Ba, Be, Co, Cr, Cu, Mn, V
40 µg/L Ag
20 µg/L As, Tl
10 µg/L Pb, Se
500 mg/L Al, Ca, Mg
200 mg/L Fe

8.17 Pulse to Analog (P/A) Calibration Solution: contains 100 ppb of all method analyte elements. Prepare by diluting a multielement stock solution to 100 ppb (calibration standard #3 may be used). To a 50 mL polypropylene centrifuge tube add 1 mL 1:1 nitric acid 500 µL of the 10 ppm stock solution and dilute to 50 mL. This solution may be used for several months as long as resulting P/A factors are consistent and in the range from 150 - 210.

9. Sample Collection, Preservation and Handling

9.1 It is important to note that MATRIX MATCHING ACID CONCENTRATIONS AND COMPOSITIONS BETWEEN STANDARDS, BLANKS AND SAMPLES IS VERY IMPORTANT IN ICP-MS ANALYSIS.

9.2 Sample holding times for preserved (HNO_3, pH<2) aqueous total, dissolved, and suspended analytes are 6 months. All sample containers must be HDPE or Teflon FEP or documented to be contaminant free. Chromic acid should **never** be used to clean any container used in ICP-MS analysis.

10. HP 4500 ICP-MS Method Data Acquisition Parameters

10.1 See the HP 4500 ChemStation Operators manual for detailed instructions on setting up the following conditions.

10.2 The following interference equations are used to correct for isobaric elemental and polyatomic interferences.

As	(1.000)(75C)-(3.127)(77C)+(2.736)(82C)-(2.760)(83C)
Cd	(1.000)(111C)-(1.073)(108C)+(0.764)(106C)
In	(1.000)(115C)-(0.016)(118C)
Pb	(1.000)(208C)+(1.000)(207C)+(1.000)(206C)
	SOME OPTIONAL ELEMENTS
Ca	(1.000)(44C)-(0.0271)(88C)
V	(1.000)(51C)-(3.127)(53C)+(0.353)(52C)
Se	(1.000)(82C)-(1.009)(83C)
Mo	(1.000)(98C)-(0.146)(99C)

Table 5: Elemental Interference Equations

10.3 Acquisition Mode: Spectrum

Points per Mass: 3

Number Replicates: 3

Integration Time: (See Table 6)
0.1 sec for all elements except As, Se, Cd and their correction masses
0.3 sec for As, Se, Cd and associated correction

masses.

10.4 Peristaltic Pump Program:

Uptake speed: 0.2 rps

Uptake time: 60 sec

Stabilization Time: 50 sec

Rinse Port Speed: 0.2 rps

Rinse Port Time: 5 sec (after standards and samples)

Optional Rinse Speed: 0.2 rps

Optional Rinse Time: 30 sec

10.5 Acquisition Masses

			Integration	Time
Mass	Element	Det. Mode	Per point	Per mass
9	Be	Auto	0.1000	0.3000
27	Al	Auto	0.1000	0.3000
45	Sc	Auto	0.1000	0.3000
50	Cr	Auto	0.1000	0.3000
52	Cr	Auto	0.1000	0.3000
53	Cr	Auto	0.1000	0.3000
55	Mn	Auto	0.1000	0.3000
59	Co	Auto	0.1000	0.3000
60	Ni	Auto	0.1000	0.3000
61	Ni	Auto	0.1000	0.3000
62	Ni	Auto	0.1000	0.3000
63	Cu	Auto	0.1000	0.3000
65	Cu	Auto	0.1000	0.3000
66	Zn	Auto	0.1000	0.3000
67	Zn	Auto	0.1000	0.3000
68	Zn	Auto	0.1000	0.3000
75	As	Auto	0.3000	0.9000
77	(As)	Auto	0.3000	0.9000
83	(Se)	Auto	0.3000	0.9000

89	Y	Auto	0.1000	0.3000
107	Ag	Auto	0.1000	0.3000
109	Ag	Auto	0.1000	0.3000
111	Cd	Auto	0.3000	0.9000
114	Cd	Auto	0.3000	0.9000
115	In	Auto	0.1000	0.3000
121	Sb	Auto	0.1000	0.3000
123	Sb	Auto	0.1000	0.3000
135	Ba	Auto	0.1000	0.3000
137	Ba	Auto	0.1000	0.3000
159	Tb	Auto	0.1000	0.3000
203	Tl	Auto	0.1000	0.3000
205	Tl	Auto	0.1000	0.3000
206-208	Pb	Auto	0.1000	0.3000
209	Bi	Auto	0.1000	0.3000

Table 6: Acquisition masses for each element with recommended integration times.

10.6 Calibrations Levels:

1 Blank

2 10 ppb for trace elements, 100 ppb for Na, K, Mg, Ca and Fe

3 100 ppb for trace elements, 1000 ppb for Na, K, Mg, Ca, and Fe

4 200 ppb for trace elements, 10,000 ppb for Na, K, MG, Ca, and Fe

Internal standard concentrations are 50 ppb for all levels, all internal standards.

10.7 Calibration Curve Fits:

All quantitation masses	y=ax+(blank)
All internal standard masses	(Excluded)
All interference correction masses	(Excluded)
All monitor masses (not for Quant)	(Excluded)

10.8 Reporting Parameters:

QC Reports	On-printer
All Other Reports	Off

11. Procedure:

11.1 Startup:

11.1.1 Verify argon supply and pressure.

11.1.2 Turn on water chiller and exhaust fan.

11.1.3 Insure that the internal standard solution bottle is adequately full (consumption is approximately 40 µL/min).

11.1.4 Verify contents of ALS rinse port reservoir(s).

11.1.5 Insure that the drain reservoir is not full.

11.1.6 Insure that all peristaltic pump tubes are in good condition and correctly clamped into the peristaltic pumps. Verify that the flow of sample and internal standard solutions through the uptake lines and into the nebulizer is free from pulsations by introducing a bubble into each line and observing its progress.

11.1.7 Initiate the plasma and allow at least 15 minutes of warm-up while scanning the mass analyzer. The tuning procedures may then be carried out during the next 15 minutes of warm-up.

11.2 **HP 4500 Tuning and Tune Verification**

11.2.1 After initiating the plasma, allow the instrument to warm up while aspirating a blank solution for at least 15 minutes. During this warm-up, select ***Tune>>Sensitivity>>Start*** so that the instrument is scanning. After the 15 minute warm-up, aspirate the HP Tune solution Reagent 8.8 (10 ppb Li, Y, Ce, Tl). Generate and evaluate the tune report. The following are suggested guidelines for an acceptable HP tune.

11.2.1.1 Tune specifications:

Sensitivity:	Li >5,000 cts/0.1 sec/10 ppb
	Y >10,000 cts/0.1 sec/10 ppb
	Tl >5,000 cts/0.1 sec/10 ppb
Precision:	Li <10% RSD (0.1 sec integration time)
	Y <10% RSD (0.1 sec integration time)
	Tl <10% RSD (0.1 sec integration time)
Oxides:	<1%
Ce^{++}	<5.0%
Background:	Li <30 cps
	Y <15 cps

Tl <15 cps

Mass Resolution: W-10% 0.7-0.8 AMU

Mass Axis: Nominal mass +/-0.1 AMU for ^{7}Li,^{89}Y and ^{205}Tl

11.3 Tune verification for Method 6020:

Since the tune criteria are poorly defined in SW-846 method 6020, the CLP tune criteria will be used for tune verification. These criteria are designed to assure that the instrument is demonstrating acceptable sensitivity, background noise, ion ratios, mass resolution and mass calibration. Analyze the tune check solution containing 100 ppb of Li, Co, In, Tl (Reagent 8.10) and evaluate against the following criteria:

HP 4500 Environmental Tune Criteria Editor

		Conc. (ppb)	Minimum response cps/(ppb)	Ion abundance Criteria (Relative to Mass 1)	
				lower	upper
Tune Mass 1 (ref).	59.0	100.0	200.0	1.0	1.0
Tune Mass 2	7.0	100.0	20.0	0.2	1.0
Tune Mass 3	115.0	100.0	100.0	0.8	2.0
Tune Mass 4	205.0	100.0	10.0	0.5	1.2
Tune Mass 5 (bkg)	102.0				

Tune Mass 5 Max Resp. 25.0 (cps)

Advanced Settings			
	Peak widths (50%) limit (Max)	Peak Widths (10%) limit (Max)	4 reps. RSD Limit (Max)
Tune Mass 1 (ref.)	0.7	1.0	5.0
Tune Mass 2	0.7	1.0	5.0
Tune Mass 3	0.7	1.0	5.0
Tune Mass 4	0.7	1.0	5.0

11.3.1 Aspirate a new rinse blank for 5-10 minutes to eliminate any carry-over into the calibration blank.

11.4 Load the method tune6020.m.

11.4.1 Run the tune6020.m method on the tune check sample, including data acquisition and data analysis. The 6020 tune report will be generated.

11.4.2 If desired, the tune report may also be generated from ***Data Analysis>>Spectrum>>Generate Tune Report***.

11.5 Aspirate a 100 ppb solution for all analyte elements and run P/A Autotune. File P/A report with tune report.

11.6 Automated Calibration, Quality Control and Sample Analysis.

11.6.1 Prepare calibration standards, blanks, spikes, samples, and QC samples as described in section 8.

11.6.2 Autobuild a QC Sequence using sequence template 6020.s. The sample list may be created using the sequence autobuilder, imported from a LIMS system, or created in Excel. See the EnviroQuant users manual for the structure of the sample list if created outside the sequence autobuilder.

11.6.3 Exit sequence autobuilder, and print the vial position guide.

11.6.4 Make any changes to the newly created sequence such as editing the sample types for spikes and spike reference samples.

11.6.5 Save the new sequence.

11.6.6 Load the ALS according to the vial position guide.

11.6.7 Select ***Sequence>>Run***.

11.7 Data Analysis and Calculations:

11.7.1 All calculations necessary to convert raw spectral intensity data into quantitative results are performed by the HP 4500 ChemStation software.

11.7.2 Any additional dilutions not accounted for in the normal sample preparation which were entered in the sample log table of sequencing will not be corrected for by the ChemStation software. These corrections should be calculated by the analyst.

11.7.3 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. In the case of Pb, quantitation is based on the sum of isotopes 206, 207, and 208 to compensate for any variation in naturally occuring isotope ratios. This is accomplished through the use of the interference correction equation for lead.

11.7.4 After completion of the sequence, the Sequence QC Summary Report should be printed and used to help evaluate any QC problems. Select ***Sequence>>View Sequence>>Summary Report.***

Mass	Element of interest
27	Aluminum
121, 123	Antimony
75	Arsenic
138, 137, 136, 135, 134	Barium
9	Beryllium
209	Bismuth (IS)
114 , 112, 111, 110, 113, 116, 106	Cadmium
42, 43, 44, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, 53 50, 54	Chromium
59	Cobalt
63, 65	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, 54, 57, 58	Iron (I)
139	Lanthanum (I)
208, 207, 206, 204	Lead
6[b], 7	Lithium (IS)
24, 25, 26	Magnesium (I)
55	Manganese
98, 96, 92, 97, 94, (108)	Molybdenum (I)
58, 60,62, 61, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
107, 109	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
120, 118	Tin (I)
89	Yttrium (IS)
64, 66, 68, 67, 70	Zinc

Table 7: Recommended Isotopes

Note: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined, although certain matrices may require the use of alternative isotopes.

[a]These masses are also useful for interference correction. [b]The Li internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

12. Quality Control:

12.1 For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area, designed for trace element sample handling must be used. Standards, samples and blanks should be exposed to the laboratory environment as little as possible. The use of preparation blanks and spikes should be used to verify the absence of sources of contamination and loss.

Note: Chromic acid must not be used for cleaning glassware for trace metals analysis.

12.2 Determine Instrument Detection Limits (IDLs) by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book.

12.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration blank, the following procedure is followed. Dilute the sample fivefold (1+4) and reanalyze with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank and instrument check standard must agree within $\pm$ 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

12.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interference are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met.

Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference

source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference correction which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used) for each instrument system are acceptable corrections for use in Method 6020.

12.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

12.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination or standard-addition analysis must be performed.

12.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

12.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

12.8.1 Check instrument calibration using a calibration blank and the initial calibration verification solution.

12.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard and the calibration blank. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

12.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed.

12.10 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations of the blank greater than 3 times the IDL, the IDL may be incorrect and should be re-evaluated.

12.11 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver.

12.12 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 10 samples.

12.12.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = relative percent difference

D_1 = first sample value

D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrument detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

13. **QC Summary: Frequency**

13.1 Initial Demonstration of performance

Establish IDLs - every three months*

Establish MDLs - every year*

*MDLs and IDLs must also be verified whenever system maintenance which may alter these values is performed such as detector replacement or significantly different tune parameters are set.

13.2 Daily Demonstration of performance

Tune	-	Before beginning analyses
Tune Verification	-	Beginning of run
Initial Calibration	-	beginning of run and when CCV fails
Internal Standard	-	Every sample
ICV	-	After calibration
ICB	-	After calibration
Dilution	-	One for each 20 samples
Spike	-	One for each 10 samples
Duplicate	-	One for each 10 samples
LCS	-	One for each batch
CCV	-	Every 10 samples
CCB	-	Every 10 samples
ICS A and AB	-	Every 12 hours

14. **Troubleshooting:**

14.1 The following section describes some commonly occurring problems and recommended solutions.

14.1.1 Poor recovery for selected analytes in spikes.

Several conditions can cause poor recovery of certain analytes in spiked samples. Ag is especially insoluble in the presence of even trace levels of Cl^-, therefore the use of HCl should be avoided whenever possible.

Several elements (Zn, As, Se, Cd) have relatively high first ionization potential and may not be as effectively ionized in samples with high concentrations of easily-ionizable elements such as Na and K. Diluting the sample if possible, or selecting an alternative internal standard with a higher ionization potential may help. Possible alternative internal standards include Ge, Te, and Au.

14.1.2 Poor calibration linearity for certain elements.

Calibration linearity can be affected by several things. Contaminated blanks, reagent water and acids are a common cause of poor linearity, especially for common elements such as Na, K, Ca, Mg, Fe, Al and Zn.

Incorrectly set P/A factors can also cause linearity problems for those elements which include analog points in the calibration curve. When analyzing samples with expected analyte concentrations above a few hundred ppb, P/A factors should be updated each day.

14.1.3 Poor agreement between standard calibration curve and QC sample.

Check dilutions and preparation for each.

Remake stock solutions.

Verify that acid composition and concentration are the same in both.

For Ca, uncorrected interference from Sr^+ in one but not the other calibration mix can cause significant interference.

14.1.4 Carryover or memory interference.

Several elements are prone to memory effects for various reasons.

Ag, Mo and Tl tend to stick to surfaces in the sample introduction system and slowly rinse into subsequent sample. Keeping the sample introduction system (sample tubing, peri pump tubing, nebulizer, spray chamber, torch and cones) clean will help minimize carryover. Also, rinsing between samples with relatively high acid concentration rinse blanks will help. If possible, avoid introducing samples or standards with concentrations of these elements above a few hundred ppb.

Use of the Babington nebulizer should also reduce carryover of these

elements.

Li, when analyzed for extended periods of time or in very high concentrations tends to accumulate on the back sides of the interface cones. Cleaning the cones will usually reduce Li background and carryover.

14.1.5 Calibration Drift over time.

Insure that the instrument is adequately warmed up before initial calibration (warm-up, while scanning in tune for 15 minutes).

Insure that laboratory temperature does not vary by more than 3^0C per hour.

Check cones for signs of sample deposits which may be affecting the size and shape of the cone orifices. Clean if necessary.

Check peri-pump tubing for signs of excessive wear or flattening.

Run SetEM. An electron multiplier which is near the end of its useful life may be changing in response over short periods of time. If running SetEM significantly changes the EM voltage from day to day, the EM should be replaced.

14.1.6 Poor internal standard recoveries in samples.

Reduction in internal standard signal is usually caused by high matrix concentration in samples (especially Na and K). Dilute the samples. It may also be desirable to tune the instrument with a matrix-matched tune solution containing appropriate levels of the matrix elements to minimize the effect of any matrix-induced suppression of ionization.

14.1.7 High relative standard deviations (RSDs) for analyte or internal standard elements during sample analysis.

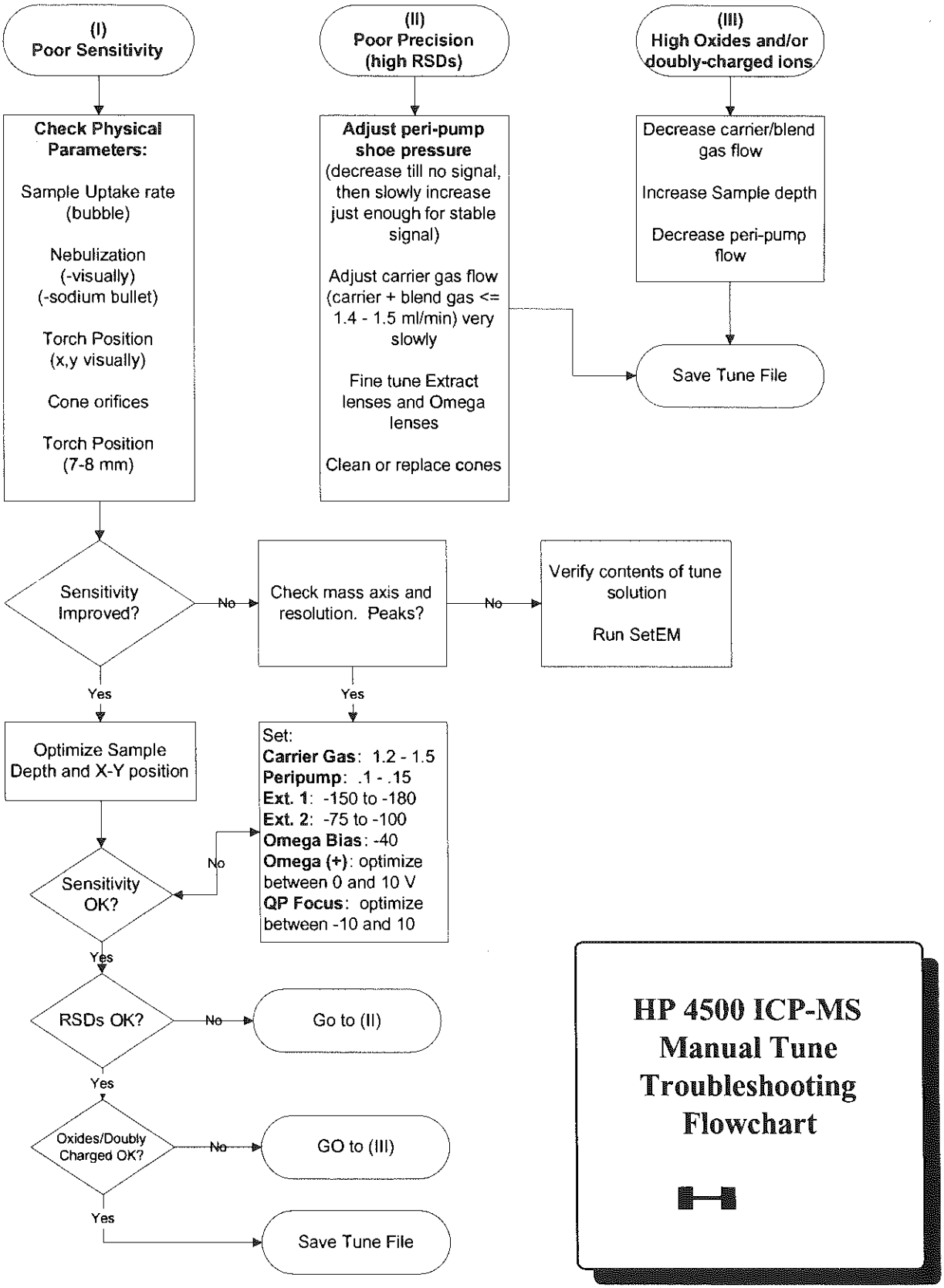
Usually caused by insufficient sample uptake or stabilization time. May be also be caused by worn peri-pump tubing or bubbles in either the sample uptake or internal standard uptake tubing. Check the connections at the ISTD addition "Y" and replace the peri-pump tubing. Shoe pressure on the peri-pump should be *just* tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).

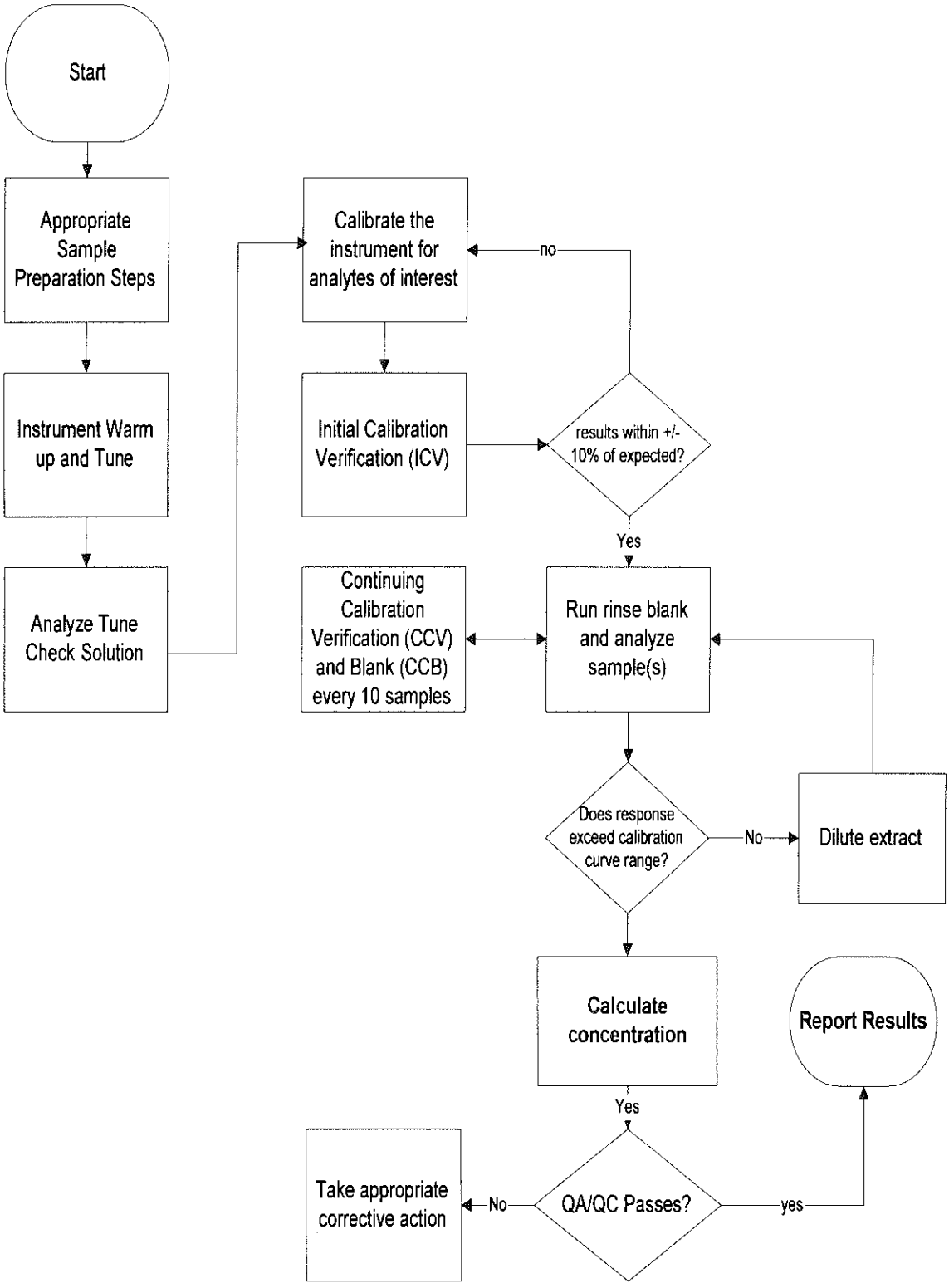
14.1.8 High RSDs during tune.

Incorrectly tuned plasma parameters such as carrier gas or blend gas flow, peri-pump speed or sample depth.

Dirty cones. Worn peri-pump tubing.

Incorrect shoe pressure on peri-pump. Should be *just* tight enough to insure a smooth flow of sample (aspirate a bubble and watch its progress through the line).


(I)
Poor Sensitivity
(II)
Poor Precision
(high RSDs)
(III)
High Oxides and/or
doubly-charged ions
Check Physical Parameters:
Sample Uptake rate (bubble)
Nebulization (-visually) (-sodium bullet)
Torch Position (x,y visually)
Cone orifices
Torch Position (7-8 mm)
Adjust peri-pump shoe pressure (decrease till no signal, then slowly increase just enough for stable signal)
Adjust carrier gas flow (carrier + blend gas <= 1.4 - 1.5 ml/min) very slowly
Fine tune Extract lenses and Omega lenses
Clean or replace cones
Decrease carrier/blend gas flow
Increase Sample depth
Decrease peri-pump flow
Save Tune File
Sensitivity Improved?
No
Check mass axis and resolution. Peaks?
No
Verify contents of tune solution
Run SetEM
Yes
Yes
Optimize Sample Depth and X-Y position
Set:
Carrier Gas: 1.2 - 1.5
Peripump: .1 - .15
Ext. 1: -150 to -180
Ext. 2: -75 to -100
Omega Bias: -40
Omega (+): optimize between 0 and 10 V
QP Focus: optimize between -10 and 10
Sensitivity OK?
No
Yes
RSDs OK?
No
Go to (II)
Yes
Oxides/Doubly Charged OK?
No
GO to (III)
Yes
Save Tune File
HP 4500 ICP-MS
Manual Tune
Troubleshooting
Flowchart


Start
Appropriate Sample Preparation Steps
Instrument Warm up and Tune
Analyze Tune Check Solution
Calibrate the instrument for analytes of interest
Initial Calibration Verification (ICV)
Continuing Calibration Verification (CCV) and Blank (CCB) every 10 samples
no
results within +/- 10% of expected?
Yes
Run rinse blank and analyze sample(s)
Does response exceed calibration curve range?
No
Dilute extract
Calculate concentration
Report Results
Yes
QA/QC Passes?
No
yes
Take appropriate corrective action

Method: KM355
Date: 03/01/93

STANDARD OPERATING PROCEDURE

Mercury Analysis Using Continuous-Flow Vapor Generator (VGA-76)

Principle
References : "VGA-76-Vapor Generation Accessory: Operation Manual."

EPA's Methods "For Chemical Analysis of Water and Waste (Manual Cold Vapor)," Method 245.1.

EPA's "Mercury in Liquid Waste (Manual Cold-Vapor Technique)," SW-846, Vol. 1A, Method 7470A.

EPA's "Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)," SW-846, Vol. 1A, Method 7471A.

Applications : This procedure explains the use of the VGA-76 cold vapor hydride generator for determination of mercury in groundwaters, aqueous wastes, extracts and solids.

Summary
Of Method : Prior to analysis, all samples must be prepared according to the procedure discussed in the preparation methods for solid and aqueous samples. In this method, mercury is reduced to the elemental state with stannous chloride and aerated from solution into a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The mercury vapor absorbs radiation at 253.7 nm and the absorbance is measured as a function of mercury concentration.

Interferences : Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide and sodium sulfide do not interfere with the recovery of added inorganic mercury.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

Interferences Cont'd :

Seawaters, brines, and industrial effluents high in chlorides may require additional permanganate (as much as 25 mL) because during the oxidation step, chlorides are converted to free chlorine, which also absorbs at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride.

Traces of potassium iodide interfere severely with the determination of mercury.

Certain volatile organic materials that absorb at this wavelength may also cause interferences. A preliminary run without reagents should determine if this type of interference exists.

Apparatus : Atomic Absorption Spectrophotometer; Varian SpectrAA-20 Plus
Varian VGA-76 (Vapor Generation Accessory)

Reagents : Deionized water
20% (w/v) Stannous Chloride: Weigh out 50 g of stannous chloride and add 65 mL HCl. Mix well. Gentle heating may be necessary in order for dissolution to take place. Bring up to final volume of 250 mL with deionized water.

Safety : All chemicals and samples should be handled with care. Lab coat, gloves and safety glasses should be worn.

Procedure :

1. Insert disc., turn on spectrophotometer and select program.

2. Insert mercury lamp into turret and set wavelength and bandwidth. Allow at least five minutes to warm up.

3. Attach the spray chamber and acetylene burner head (equipped with brackets). Mount vapor generation accessory (VGA-76) in front of spray chamber. Place the flue in proper slots so it is situated directly below the hood.

4. Hook up power supply, argon connection and waste hose to the VGA.

5. Optimize signal by adjusting wavelength and aligning lamp without flow-through cell.

Procedure Cont'd :

6. Place flow-through mercury cell on the brackets of the burner head. Make sure the black tubing between the flow-through cell and the gas-liquid separator is connected. Attach exhaust tubing to the hood and drying light to the flue. Reoptimize signal by aligning the cell vertically and horizontally with the vertical and horizontal burner controls. Then by hand, align the cell in the path of the light for maximum intensity.

7. Hook up pump tubing, place uptake capillary tubes into a beaker of deionized water and turn VGA-76 on. Check to make sure low gas pressure light (on right side of VGA-76) is not on. Turn pressure bar to the closed position and check to see if deionized water is being drawn into the system. Measure uptake rates of all three pump tubes using a graduated cylinder and stop watch. Take three reading for each tube to ensure consistency. The uptake rate of the two smaller tubes should be about 1.0-1.3 mL per minute. The uptake rate for the larger sample tube should be about 7-10 mL per minute. The uptake rates may be adjusted with the pressure adjusting screws located on the pressure bar.

8. Place the two reagent containers on the left side of the VGA-76 tray, with the stannous chloride solution behind the deionized water container. Place the two smaller capillary tubes in their respective containers and leave the large sample tube in the deionized water.

9. After the instrument has been set up, add the hydroxylamine hydrochloride to the samples and standard. Mix thoroughly until clear. Place the sample uptake tube in the lab method blank. Wait approximately 45-60 seconds for the system to stabilize, then press the INSTR'MT ZERO key.

10. Before analyzing samples, the blank and standards must be analyzed in order to establish a standard curve. Proceed to the CALIBRATION page. Place the sample uptake tube in the lab method blank and press the blue **READ** key. The program will be delayed (for the number of seconds set on the instrument parameters page) and then the instrument will take three readings and print the results. Proceed to the next standard using the same technique.

11. After all the standards have been analyzed, the instrument will construct a calibration curve, proceed to the ANALYTICAL RESULTS page, and begin analyzing the samples.

Calculations :

1. Construct a calibration curve by plotting the absorbance of the standards versus concentration (ug/L) of mercury. Use absorbance of the sample to determine the concentration of mercury.

2. Solids: Since the mercury values of the samples are in ug/L, an additional calculation must be done in order to convert the values to mg/kg:

$$\text{Sample conc.(ug/L)} \times \frac{\text{final vol. of sample (L)}}{\text{wt. used (g)}}$$

Quality Control :

1. A minimum of one spike and one duplicate must be performed for every ten samples analyzed. If the recovery of the spike is not within 75-125% and the relative percent difference of the duplicate is above 20, then the problem must be isolated, corrected and documented.

2. A laboratory method blank must be prepared with each sample batch. If contamination is detected, the problem must be isolated, corrected and documented.

3. Before analyzing samples, initial calibration verification must be performed (ICV and ICB). Continued calibration verification samples must be analyzed at least every ten samples and again at the end of the run.

Test results on "SDWA" samples which are confirmed as failing an MCL must be brought to the attention of the analyst's supervisor (or equivalent)immediately. The supervisor will then notify the client of the MCL failure by telephone without delay.

Lowest Reporting Level :

0.0005 mg/L or 0.5 mg/kg standard D.L.
0.0002 mg/L or 0.1 mg/kg low level D.L.

Method No.: KM7471A
Issue Date: 3/01/93
Last Revision: 6/18/98

STANDARD OPERATING PROCEDURE
for
Analysis of Mercury in Soil, Solid or Semisolid Waste

1. Principal References:

1.1 "Mercury in Solid or Semisolid Waste," SW-846, 3rd Edition, Update III, Method 7471A, U.S. EPA, December, 1996.

1.2 "Mercury in Liquid Waste," SW-846, Method 7470A, U.S. EPA, December, 1996.

1.3 "Methods For Chemical Analysis of Water and Waste," EPA-600/4-79-020, Method 245.1, U.S. EPA, December, 1996.

1.4 "VGA-76-Vapor Generation Accessory Operation Manual, Varian, March, 1988.

2. Scope & Application:

2.1 This procedure describes the determination of total mercury (organic and inorganic forms) in soils, sediments, bottom deposits and sludge-type materials. All samples must be digested prior to analysis. This procedure uses the Varian VGA-76 cold-vapor generator.

3. Summary Of Method:

3.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedure discussed in Section 9.2 of this method.

3.2 Mercury is reduced to the elemental state with stannous chloride and aerated from solution into a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The mercury vapor absorbs radiation at 253.7 nm and the absorbance is measured as a function of mercury concentration.

3.3 The typical Instrument Detection Limit (IDL) for this method is 0.0002 mg/L.

4. Interferences:

4.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide (as sodium sulfide) do not interfere with the recovery of added inorganic mercury in reagent water.

4.2 Copper has also been reported to interfere, but copper concentrations as high as 10 mg/kg had no effect on recovery of mercury from spiked samples.

4.3 Samples high in chlorides may require additional permanganate (as much as 25 mL). This is because chlorides are converted to free chlorine during the oxidation step which also absorbs radiation of 253 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent.

4.4 Certain volatile organic materials that absorb at this wavelength may also interfere. A preliminary run without reagents should determine if this type of interference exists.

5. Apparatus & Equipment:

Atomic Absorption Spectrophotometer, Varian SpectrAA-20 Plus
Varian VGA-76 (Vapor Generation Accessory)
Flow-through (absorption) cell
Mercury hollow cathode lamp
200 mL tall beakers
Aluminum foil
Watch glasses
Water bath
100 mL volumetric flasks, class A
250 mL volumetric flasks, class A
100 mL graduated cylinders
Spatulas, wooden or stainless steel
OPTIFIX® acid dispenser
Eppendorf adjustable calibrated pipetters and tips
10 - 100 µL
100 - 1000 µL
1000 - 2500 µL
Talc-free gloves

6. Standards and Reagents:

Reagent water equivalent to ASTM Type 1 (ASTM D1193), >18 Megaohm/centimeter resistivity.

Nitric acid, concentrated "Trace Metal," 2.5 L in glass, (Fisher cat. #A509-212)

Hydrochloric acid, concentrated "Trace Metal," 2.5 L in glass, (Fisher cat. #508-212)
Sulfuric acid, concentrated "Select," 2.5 L in glass (VWR cat. #MK-555-746)

Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

Potassium permanganate, crystals, 99% min, ACS (VWR cat. #MK-706-804)

Stannous chloride, crystals, ACS (VWR cat. #MK-817-604)

Sodium chloride, granular, ACS (VWR cat. #MK-753-206)

Hydroxylamine hydrochloride, crystals, ACS (VWR cat. #MK-525-812)

Mercury stock standard (for calibration and spiking) 1000 mg/L (Spex cat. # PLHG4-2Y). This standard comes with a certificate of analysis and has an expiration date of one year.

Mercury stock standard (for calibration verification) 1000 mg/L (SPC cat. # 140-001-8051). This standard comes with a certificate of analysis and has an expiration date of one year.

Mercury working standards, 1000 µg/L: Add 100 µL of 1000 mg/L Mercury stock standard using an adjustable 100 µL calibrated pipetter to a 100 mL volumetric flask ¾ full with reagent water. Add 2 mL of concentrated HNO_3 with the OPTIFIX acid dispenser and bring up to volume with reagent water . Store in a 125 mL nalgene bottles, label one bottle calibration standards and spikes and the other bottle ICV/CCV. These standards expire in 30 days. Standards prepared from working standards must be made fresh daily.

Potassium permanganate solution, 5% (w/v): Dissolve 25g of potassium permanganate in 500 mL of reagent water. Mix well and store in a glass bottle. This solution expires in 30 days.

Stannous chloride solution, 20% (w/v): Dissolve 50g of stannous chloride with 65

mL of concentrated hydrochloric acid in a 250 mL volumetric flask. Mix well until all of the salt is in solution. Bring up to volume with reagent water. This solution expires in 30 days.

Sodium chloride - hydroxylamine hydrochloride solution: Dissolve 60g of sodium chloride and 60g of hydroxylamine hydrochloride in 500 mL of reagent water. Mix well and store in a glass bottle. This solution expires in 30 days.

7. **Safety:**

7.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices should be practiced at all times.

7.2 Safety glasses and acid-resistant gloves should be worn at all times when handling samples or reagents, or when in the vicinity of others handling these items.

7.3 The Varian SpectrAA-20 Plus is fully interlocked to prevent the user from harmful electrical voltages, ultraviolet radiation, and other hazards. At no time should the operator attempt to disable these interlocks or operate the instrument if any safety interlock is suspected to be disabled.

7.4 Spilled samples and reagents should be cleaned up from instrument and laboratory surfaces immediately. Acid spills should be neutralized with sodium bicarbonate solution before cleanup.

8. Sample Collection, Preservation and Handling

8.1 Plastic and glass containers free of contamination are both suitable.

8.2 Non-aqueous samples shall be refrigerated when possible, and analyzed within 28 days of collection.

9. **Procedure:**

9.1 Standard preparation: Transfer 0, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 mL aliquots of the mercury working standard to a series of 200 mL beakers labeled Blank, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 µg of mercury respectively. Transfer 3.0 mL of the second source mercury working standard to a 200 mL beaker labeled ICV/CCV

3.0 µg/L. Add enough reagent water to each beaker to make a final volume of 10.0 mL. Add 5 mL of aqua regia water and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxalamine solution to reduce the excess permanganate just before analysis.

9.2 Sample preparation: Weigh a 0.5-0.6 g aliquot of well homogenized sample and place in the bottom of a 200 mL beaker. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min. in a water bath at 95°C. Cool, then add 55 mL of reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate just before analysis.

CAUTION: Perform this addition under a hood, as Cl_2 could be evolved.

9.3 Insert disk, turn on spectrophotometer and select program.

9.4 Insert mercury lamp into turret and set wavelength to 253.7 nm and bandwidth to 0.5 nm. Allow at least five minutes to warm up.

9.5 Attach the spray chamber and acetylene burner head (equipped with brackets). Mount vapor generation accessory (VGA-76) in front of spray chamber. Place the flue in proper slots so it is situated directly below the hood.

9.6 Attach power supply, argon connection and waste hose to the VGA.

9.7 Optimize signal by adjusting wavelength and align the lamp without flow-through cell.

9.8 Place the flow-through cell on the brackets of the burner head. Make sure the black tubing between the flow-through cell and the gas-liquid separator is connected. Attach exhaust tubing to the hood. Reoptimize the signal by aligning the cell vertically and horizontally with the vertical and horizontal burner controls. Align the cell in the light path for maximum intensity.

9.9 Attach pump tubing, place uptake capillary tubes into a beaker of reagent water and turn on VGA-76. Check to make sure "low gas pressure" light (on right side of VGA-76) is not on. Turn pressure bar to the closed position and ensure that the reagent water is being drawn into the system. Measure uptake rates of all three pump tubes using a graduated cylinder and stop watch. Take three reading for each tube to ensure consistency. The uptake rate of the two smaller

tubes should be about 1.0-1.3 mL per minute. The uptake rate for the larger sample tube should be about 7-10 mL per minute. The uptake rates may be adjusted with the pressure-adjusting screws located on the pressure bar.

9.10 Place the two reagent containers on the left side of the VGA-76 tray. Place the stannous chloride solution behind the reagent water container. Place the two smaller capillary tubes in their respective containers and leave the large sample tube in the reagent water.

9.11 After the instrument has been set up, add the hydroxylamine hydrochloride to the samples and standards. Mix thoroughly until clear. Place the sample uptake tube in the calibration blank. Wait approximately 45-60 seconds for the system to stabilize, then press the "INSTR'MT ZERO" key.

9.12 Before analyzing samples, the blank and standards must be analyzed to establish a calibration curve. Proceed to the CALIBRATION page. Place the sample uptake tube in the calibration blank and press the blue "**READ**" key. The program will be delayed (for the number of seconds set on the instrument parameters page) and then the instrument will take three readings and print the results. Proceed to the next standard using the same technique.

9.13 After all the standards have been analyzed, the instrument will construct a calibration curve. Proceed to the ANALYTICAL RESULTS page and begin analyzing the samples.

10. Calculations:

10.1 Construct a calibration curve by plotting the absorbance of the standards versus concentration (µg/L) of mercury. Use absorbance of the sample to determine the concentration of mercury. Each calibration curve must have a blank and four standards and a correlation coefficient (r = 0.995) or better. Dilute and rerun all samples that exceed the calibrated range.

10.2 Solids: Since the mercury concentrations in the samples are in ug/L, an additional calculation must be performed to convert the values to mg/kg:

$$\text{Sample (mg/kg)} = \frac{\text{Sample conc.(ug/L) x final vol. of sample (L)}}{\text{wt. used (g)}}$$

$$\text{Sample (mg/kg dry sample)} = \frac{\text{Sample (mg/kg)}}{\text{\% Total solids}} \times 100$$

% total solids in sample as determined by KAR SOP KG462

11. Quality Control:

11.1 A minimum of one spike must be performed for every ten samples. If the recovery of the spikes are not within 75-125%, check the LFB recovery to determine if the loss was due to the digestion process. If the LFB is within the window (± 25%), flag the data as possible matrix effect.

11.2 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 10 samples.

11.2.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = relative percent difference

D_1 = first sample value

D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrument detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

11.3 A Laboratory Method Blank (LMB) must be prepared with each sample batch. If contamination is detected the problem must be isolated, corrected and documented. The samples must be redigested and reanazlyzed.

11.4 A Laboratory-Fortified Blank (LFB) must be prepared with each sample batch. If recovery is not within 75 - 125% the problem must be isolated, corrected and documented. The samples must be redigested and reanalyzed.

11.5 Before analyzing samples, initial calibration verification must be performed (ICV and ICB). Continuing calibration verification samples must be analyzed at least every ten samples and again at the end of the run. The ICV/CCV must be made from a different working standard than the calibration standards. The recovery must be within ± 10 of the true value. If not, terminate the run, correct the problem, recalibrate and rerun any samples that were run since the last good ICV/CCV. The ICB/CCB should be less than the reporting limit. If not, terminate the run, correct the problem, recalibrate and rerun any samples that were run since the last good ICB/CCB.

11.6 Lowest Reporting Level: 0.5 mg/kg standard D.L.
0.1 mg/kg low level D.L.

11.7 Typical Run Sequence:
Warm-up instrument for 15 min.
Instrument zero
Blank
0.2 µg/L std.
0.5 µg/L std.
1.0 µg/L std.
2.0 µg/L std.
5.0 µg/L std.
10.0 µg/L std.
ICV "second source"
ICB
Analyze 10 samples
CCV (after every 10 samples and at the end of a run)
CCB (after every 10 samples and at the end of a run)

12. Preventative Maintenance

12.1 Record all maintenance in the AA-20 maintenance logbook.

12.2 Each day check the following:
- Argon supply - replace when needed.
- Waste container - empty when needed.
- Sample pump tubing - replace when needed.
- Liquid-gas separator - clean when needed.
- Optical alignment - adjust for optimal signal

12.3 At the end of a run, rinse all pump tubing with reagent water for 10 minutes. Pump air into tubing for storage.

12.4 Refer to Varian's maintenance manual when other problems arise.

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STANDARD OPERATING PROCEDURE

The Determination of Total Cyanide in Water

1.0 Principal References

1.1 *Standard Methods*, 18th edition, Method 4500-CN^- A,B,C,K; EPA SW-846, Methods 9010B and 9014.

2.0 Application

2.1 This method can be applied to all types of aqueous samples. The linear range for this method is 0.005-0.400 mg/L. The practical quantitation limit (PQL) for this method is 0.005 mg/L.

3.0 Summary of Method

3.1 A portion of the sample is pre-treated, if necessary, and then distilled under strongly acidic conditions. Any cyanide in the sample is converted to HCN gas which is immediately swept from the reaction vessel and captured in a hydroxide trapping solution as the free cyanide anion. A portion of each distilled standard and sample is then color-developed manually and read spectrophotometrically at 578 nm.

4.0 Interferences

4.1 Sulfide will give a positive interference. The addition of bismuth nitrate solution to the sample in the reaction vessel will help remove the interference. The addition of lead carbonate directly to the trapping solution should be done only when the bismuth nitrate treatment is ineffective. Diluting of the sample coupled with the prescribed treatment is permitted.

4.2 Nitrate and/or nitrite in the presence of some organic compounds may form HCN during the distillation process. The addition of a sulfamic acid solution will prevent this. Because the analyst may be unaware of their presence, the addition of sulfamic acid is done routinely with all wastewaters and wastes.

4.3 Some volatile organics will also distill over and consume large amounts of the chloramine-T reagent. It is absolutely imperative that the analyst verify that there is an excess of chlorine available for the complete conversion of cyanide to cyanogen chloride during color development.

4.4 If a strong oxidizing agent such as chlorine is known to be present in the wastestream at the time of collection, an excess of **ascorbic acid must NOT be added** prior to preservation. Add sufficient amounts of sodium arsenite to reduce the oxidizer to a non-detect level.

5.0 Sample Handling

5.1 Because some forms of cyanide are easily converted to HCN gas when exposed to air, collect one liter of sample containing 12 pellets of sodium hydroxide. The analysis must performed within 14 days, and the sample must be stored at 4°C.

6.0 Apparatus and Equipment

6.1 Cyanide MIDI distillation apparatus (Kontes Glass)
Spectrophotometer (vis), 2.5 cm pathlength
Cuvette, 2.5 cm
Vortex mixer
20 x 150 mm disposable test tubes
Plastic storage tubes, 50 mL

7.0 Preventive Maintenance

7.1 Wipe up all reagent spills on unit surfaces immediately to prevent corrosion.
7.2 Change distillation tubing on all ten assemblies every six months or as needed.

8.0 Chemicals

8.1 All chemicals used for the preparation of reagents must be Reagent Grade quality or better.

8.2 Lead acetate paper
Potassium cyanide, KCN
Potassium iodide-starch indicator paper
Sodium hydroxide pellets, NaOH
Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$
Sulfamic acid, H_2NSO_3H
Hydrochloric acid, HCl
Sulfuric acid, H_2SO_4
Silver nitrate titrant, certified, 0.01N
Magnesium chloride, $MgCl_2 \cdot 6H_2O$
Sodium arsenite solution, 0.01M (store at 4°C)
Ethylenediamine
Chloramine-T
Pyridine
Barbituric acid
p-dimethylaminobenzalrhodanine indicator
Glacial acetic acid
Sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_2O$

9.0 Safety

9.1 The analyst should assume that all samples received for cyanide analysis do in fact contain cyanide-bearing compounds and should be handled with the appropriate caution. Hydrogen cyanide is a highly toxic gas, and reasonable precautions should be taken to prevent its release.

9.2 The distillations should be performed in or near a fume hood. During distillation, all joints in the apparatus should be checked periodically to prevent the release of HCN into the lab.

9.3 Sulfuric and hydrochloric acid are highly corrosive mineral acids. Handle them with care and wear a labcoat, safety glasses and other dermal protection against spills. Hydrochloric acid is also very volatile. Prevent the release of corrosive fumes by handling in a fume hood.

9.4 Pyridine is a volatile, toxic solvent which should be handled in a fume hood with gloves.

9.5 Ethylenediamine is a corrosive, volatile organic base. Do not breathe fumes. Handle only in a fume hood wearing dermal protection.

10.0 Preparation of Reagents

Note: For the analysis of samples involving Level 4 QC requirements, record the preparation of all reagents containing acids or solvents in the Level 4 Reagent Prep Log. Record the date, analyst initials, name of reagent, and lot numbers of all acid or solvents used in the prep.

Note: For the analysis of samples involving Level 4 QC requirements, any variable pipettor used in the preparation of reagents must be calibrated prior to each use. Fixed-volume pipettors are preferred and must have their calibration checked at least weekly.

10.1 Bismuth Nitrate Solution
In a 1L beaker dissolve 30.0g of bismuth nitrate into 100 mL of deionized water, add (stirring) 250mL of glacial acetic acid and dilute to 1L with deionized water. Store in a 1L plastic container, and prepare fresh every six months.

10.2 Sulfamic Acid Solution
Dissolve 100g of sulfamic acid in deionized water and dilute to 1L. Store in a 1L plastic container, and prepare fresh every six months.

10.3 Magnesium Chloride Solution
Dissolve 510g of $MgCl_2 \cdot 6H_2O$ into 1L of deionized water. Store in a 1L plastic container, and prepare fresh every six months.

10.4 Sodium Hydroxide Diluent (0.25N)
Dissolve 10.0g of NaOH pellets in 900mL of deionized water in a 1L volumetric flask and dilute to the mark. Store in a 1L plastic container, and prepare fresh every six months.

10.5 Chloramine-T Solution
Dissolve 0.1g per 10mL of deionized water in a 50mL Erlenmeyer flask. Make up fresh daily.

10.6 Sulfuric acid, 1:1 (18 N)
In an ice water bath on a stir plate, dilute 500mL of conc. sulfuric acid into 500mL of deionized water. Add the acid to the water in three equal portions, allowing time for cooling between each addition. Store in a 1L plastic container, and prepare fresh every six months.

10.7 Ethylenediamine Solution, 5%
In a fume hood, dilute 5mL of ethylenediamine into 95 mL of deionized water. Store in amber glass at 4°C. Make up fresh as needed.

10.8 Phosphate Buffer Solution
Dissolve 138g of sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_2O$, into 1L of deionized water. Store in a 1L plastic container and keep refrigerated to discourage bacterial growth. Make up fresh every six months.

10.9 Pyridine-Barbituric Acid Reagent
Note: This preparation of this reagent will take much less time if the following procedure is followed. Transfer 6.0g of barbituric acid into a dry 100mL volumetric flask. Add a 1" magnetic stir bar and then wet the powder thoroughly with 5-10mL of deionized water. Allow the mixture to stir for at least 10 minutes until it is homogeneous. Then add 30mL of pyridine while stirring continues. When this mixture appears homogenous, add 6mL of conc. HCl and then dilute to volume with deionized water. The reagent begins as an opaque slurry but eventually becomes a clear, light-yellow solution. Store in a 250mL amber bottle and keep refrigerated. Make up fresh weekly.

10.10 Benzalrhodanine Indicator Solution
In 100mL of acetone, dissolve 20mg of p-dimethyl-aminobenzalrhodanine. Store in 250mL amber glass bottle and make up fresh every two years.

10.11 Silver Nitrate Titrant, 0.01920N (1.00 mL = 1.00 mg CN^-)
Purchase a certified standard (VWR, Cat. #VW3360-01). Store in original glass amber container at room temperature. Purchase a new standard annually.

11.0 Preparation of Standards

Note: For the analysis of samples involving Level 4 QC requirements, any variable pipettor used in the preparation of standards must be calibrated prior to each use. Fixed-volume pipettors are preferred and must have their calibration checked at least weekly.

11.1 Cyanide Primary Stock Standard, ≈1000 mg/L
Dissolve 1.255g KCN and 1g KOH in deionized water, dilute to 500mL and mix well. Store in a 500mL plastic container at 4°C. Prepare fresh when standardized concentration falls below 950 mg/L.

11.2 Standardization of the ≈1000 mg/L Stock

Add 50 mL of deionized water to a 250mL Erlenmeyer flask and pipet 10.0mL of the Stock Standard. Add 5 drops of the benzalrhodanine indicator solution and titrate with the 0.0192N certified silver nitrate titrant to a salmon pink color. Repeat and calculate the average. Titrate a blank and use the following equation to calculate the actual concentration of the stock standard:

$$\text{Stock } CN^- \text{ conc. (mg/L)} = (A - B) \times 100$$

where A = avg. mL titrant for stock
B = mL titrant for blank

11.3 Cyanide Intermediate Stock Standard, ≈10.0 mg/L

Dilute 2.0mL of the 1000 mg/L primary stock to 200mL volumetrically with deionized water and mix well. Do not store; use immediately to prepare working stock standard.

11.4 Cyanide Working Stock Standard, 1.0 mg/L

Pipet 10.0mL of the 10.0 mg/L intermediate stock to 100mL volumetrically with deionized water and mix well. Do not store; use immediately to prepare calibration standards for distillation.

11.5 Cyanide Calibration Standards (must be distilled to correct for negative bias)

Prepare a set of calibration standards with cyanide concentrations of 0, 0.005, 0.020, 0.040, 0.100, 0.200, 0.300 and 0.400 mg/L by transferring 0, 0.25, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 mL of the working stock to separate 50mL distillation tubes. Dilute to the 50mL mark on each tube and distill just like samples.

NOTE: In each case, the actual concentration of each calibration standard must be calculated from the standardized value of the 1000 mg/L stock.

11.6 Spiking Stock Standard, 1000 mg/L

Prepare a second primary stock standard as described above from a second KCN source. Standardize and store as above.

11.7 Spiking Standard, ≈5.0 mg/L

Dilute 1.0mL of the spiking stock standard to 200mL in a volumetric flask just prior to distillation. A 1.0mL addition of this solution to 50mL of sample represents approx. a 0.1 mg/L spike addition, depending on the exact concentration of the stock as standardized.

11.8 Lab Control Standard, 0.05 mg/L

Prepare a lab control standard from a source other than that of the calibration standards. Dilute 1.0mL of the 1000 mg/L Spiking Stock Standard to 100mL with deionized water and mix well. Dilute 10.0mL of this intermediate standard to 100mL with deionized water and mix well. Transfer 2.5mL of this working standard to its own 50mL distillation tube and bring up to volume with deionized water. Distill with samples.

12.0 Procedure

12.1 Pre-treatment of Samples

12.1.1 Test for sulfide. Dip a strip of lead acetate paper in the sample. If a brownish color results, add a 5 mL portion of bismuth nitrate to the 50 mL sample before distillation.

12.1.2 Treatment for aldehydes (only if sample has an aldehyde odor). Add 2 mL of 3% ethylenediamine to the 50 mL sample before distillation.

12.1.3 Test for oxidizers (chlorine). Dip a strip of starch-iodide into the 50 mL sample. If a blue color appears, add 1 mL portions of sodium arsenite solution until the sample tests negative. Record the amount of arsenite solution needed.

12.2 Distillation Procedure

Note: Prepare and distill a complete set of calibration standards (section 11.5) for each analytical batch of samples. This will include a high and low standard.

12.2.1 Gently mix the sample and transfer 50.0mL of sample (or an appropriate dilution) to a distillation tube.

12.2.2 Transfer 50.0mL of the 0.25N sodium hydroxide solution to a scrubber tube.

12.2.3 Turn on the cold water which will circulate through the cold fingers. Be sure that flow does not exceed the 8-10 setting on the flow meter.

12.2.4 Immediately assemble each distillation tube with its own scrubber tube using the rest of the distillation apparatus, making sure all joints are wetted and secure.

12.2.5 Make sure each of the individual flow controllers are in the OFF position. Turn on the vacuum pump to start a slow stream of air through the MIDI system. The flow rate in the distillation tube should be at least two bubbles per second.

NOTE: Make sure there is enough water in the pump trap so that the glass tube is below the water surface and nearly touching the floor of the flask.

12.2.6 Adjust each flow controller so that uniform bubble pattern is seen in each scrubber tube.

NOTE: The fritted glass end of the scrubber apparatus must be intact so that an extremely fine pattern of bubbles is formed. Do not use scrubbers which produce large bubbles.

12.2.7 Turn the power switch ON and set the heater/timer to 105 minutes. This will allow the block to begin heating while the following reagents are added. Record this start time of the distillation in the logbook.

12.2.8 Add 5mL of the bismuth nitrate solution through the inlet tube to any aqueous samples that tested positive for sulfide.

12.2.9 Add 2 mL of the sulfamic acid solution through all inlet tubes.

12.2.10 Carefully add 5mL of the 1:1 sulfuric acid solution through all inlet tubes.
12.2.11 Add 2mL of the magnesium chloride solution to all inlet tubes and rinse each with a small addition of deionized water.
12.2.12 Turn the heating mantle setting to 126°C. Allow full refluxing for 90 minutes.

NOTE: Keep readjusting and checking the flow to each scrubber as the reaction mixture heats. The flow will change during the distillation portion of the analysis.

12.2.13 Record all prep data in the Cyanide logbook. Note all dilutions and unique observations.
12.2.14 After 90 minutes of reflux, turn off the mantle and let the reaction tubes cool for 15 minutes. Record the stop time of the distillation in the logbook.
12.2.15 Transfer each scrubber solution to its own labeled 50mL plastic storage tube. If quantitation will not be taking place immediately, store scrubber solutions at 4°C until quantitation.

NOTE: It is most efficient to have the left side of the unit right next to a sink for this "transfer and rinse-down" portion of the analysis. Turn off all the flow controllers except the left-most one. Remove each scrubber apparatus in turn and attach it to the left-most flow position for the transfer and rinse-down. After pouring off the scrubber solution, rinse the flow tube with 10% HCl, then deionized water. Then dump that rinse mixture and rinse the entire apparatus with water. The remaining distillation tubes and scrubber tubes are rinsed and washed with soapy water separately.

12.2.16 Release the vacuum on the trap and then turn the vacuum pump OFF.
12.2.17 Dispose of the sample waste (arsenite-treated solutions go to heavy metal waste) and clean the entire apparatus with 10% HCl followed by large volumes of deionized water. Wipe the surface of the cold finger; rinsing alone is not always sufficient.
12.2.18 Quantitate the distillates within 48 hours of generating them.

12.3 Color Development and Quantitation

12.3.1 Set the wavelength of the spectrophotometer to 578nm and allow the unit to warm up.
12.3.2 Transfer 8.0mL of each of the distilled standards and sample distillates to its own 20x150 mm test tube.
12.3.3 Add 2.5mL of room temperature phosphate buffer to all calibration standards and samples.
12.3.4 In a fume hood, add 0.3mL of the chloramine-T reagent to all tubes and vortex.
12.3.5 Check each tube with the starch-iodide paper. If an indigo color is not observed, keep adding 0.3mL aliquots of the chloramine-T reagent until an excess of chlorine is observed. If more than 1.0 mL is needed, adjust the final result for dilution.
12.3.6 In a fume hood, add 1.0mL of the pyridine-barbituric acid reagent to each tube, standards first and samples last. Vortex each tube after the addition.

12.3.7 Allow 8 minutes for complete color development.
12.3.8 Standardize the instrument using the 0 mg/L standard.
12.3.9 Record the absorbance of each standard and sample in the Cyanide logbook.
12.3.10 Samples which exceed the absorbance of the highest standard must be diluted with the 0.25N NaOH diluent and redeveloped. If a dilution greater than eight times the high standard is needed, redistill a smaller sample portion.

13.0 Data Analysis and Reporting

13.1 Construct a calibration curve using all eight standards with a statistical calculator having linear regression capability. The correlation coefficient of the curve must be greater than or equal to 0.997. If the correlation coefficient does not meet this acceptance criterion, distill a new set of calibration standards and reanalyze the entire analytical batch.

13.2 Obtain sample results directly off the curve. Apply any necessary dilution factors:

$$\frac{\text{Result of diluted sample} \times \text{(Final dilution volume)}}{\text{(Volume of sample diluted)}} = \text{Final result}$$

13.3 Record in the lab notebook each sample result exactly as it will be reported, including any applicable condition codes for any data that must be qualified (see Table 1).

13.4 Submit the data to a qualified analyst for peer-review. Make any necessary corrections found in peer-review.

13.5 Enter the sample results and QC data into the LIMS data system. Print a copy of the data entry table and submit to an analyst for data entry peer-review. Make any necessary corrections.

14.0 QA/QC

14.1 A Lab Method Blank (LMB) must be distilled and analyzed for every batch of samples and every twenty samples thereafter. If the result of any LMB is not less than 0.005 mg/L, the analyst must reanalyze the distilled blank to confirm the failure. If the failure is confirmed, the entire batch of samples must be redistilled and reanalyzed.

14.2 A duplicate analysis must be distilled and analyzed with every analytical batch at a frequency of every ten samples. Calculate the relative percent difference (RPD) as follows:

$$RPD = 100 (| X_1 - X_2 |) / m$$

where X_1 = first duplicate result
X_2 = second duplicate result
m = arithmetic average of X_1 and X_2

If the RPD is greater than 15%, the analyst must consult the laboratory supervisor for possible reanalysis and/or reporting of a matrix effect for that individual sample or the entire QC batch.

14.3 A matrix spike analysis must be distilled and analyzed with every analytical batch at a frequency of every ten samples. Calculate the matrix spike recovery as follows:

$$\% \text{ Recovery} = 100 (M - S) / a$$

where M = spiked sample result, mg/L
S = sample result, mg/L
a = matrix spike addition, mg/L

If the matrix spike recovery falls outside a range of 85-115%, the analyst must first confirm the failure by reanalyzing. If confirmed, consult the laboratory supervisor for possible reanalysis and/or reporting of a matrix effect for that individual sample or the entire QC batch.

14.4 A Lab Control Standard (LCS) originating from a second source and falling near the 0.05-0.10 mg/L range must be distilled and analyzed every analytical batch and every twenty samples thereafter. Calculate the percent recovery as follows:

$$\% \text{ Recovery} = 100 (C) / t$$

where C = the control standard result, mg/L
t = the true value of the standard, mg/L

If the percent recovery is less than 85% or greater than 115%, the failure must be confirmed by reanalysis. If confirmed, the entire batch must be redistilled and reanalyzed on a new calibration.

15.0 Method Performance

15.1 A single-operator MDL study for this analysis obtained the following results:

True value (μg/L)	Replicate results (μg/L)	Mean (μg/L)	Std. dev.	MDL
5	4.7, 4.3, 4.5, 4.5, 4.9, 4.1, 4.3	4.5	0.27	0.85
5	5.0, 5.0, 5.2, 5.2, 5.2, 5.0, 5.2	5.1	0.11	0.34

16.0 Reporting Limitations

16.1 The reporting limit for this analysis will be 0.005 mg/L. Do not report values past the third decimal place, and do not report values with more than three significant figures.

TABLE 1

LIMS CONDITION CODES

CODE	REPORT COMMENT
AH	Result is from second analysis performed past holding time.
AM	Analysis could not be performed clue to matrix difficulties.
AP	Apparent matrix effect observed; result is approximate.
AZ	Analysis cannot be performed on this sample type.
DA	Sample container broken; data is approximate.
DE	Result is approximate due to sample matrix difficulty.
DL	Elevated detection limit due to limited sample amount.
DM	Elevated detection limit due to sample matrix interference.
DT	Elevated detection limit due to unusual sample type.
FS	Analysis performed on filtered sample.
IE	Inconclusive result due to matrix effects.
IR	Inconclusive result due to matrix interference.
IS	Insufficient sample to achieve requested detection limit.
OH	Analysis placed on hold by client
PE	Problem encountered during analysis; result is approximate.
QM	Apparent matrix effect; result is approximate.
QQ	Data failed Quality Control; result is approximate.
RA	Result is approximate due to matrix interference.
SA	Sample was lost due to Laboratory accident.
SB	Sample bottle was received broken
SC	Improper sample container; result is approximate.
SD	Insufficient sample amount; result is approximate.
SF	Sample received frozen; result is approximate
SP	Improper sample preservation; result is approximate.
SQ	Insufficient sample amount to perform the analysis.
SR	Sample received past holding time; result is approximate.
SS	Analysis ordered past holding time; result is approximate.
ST	Sample analyzed past holding time; result is approximate.
SU	Sample received in unusual container.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: David R. Alkema Date: 10/12/00
Dave Alkema

Supervisor: Michael Jaeger Date: 10/12/00
Michael Jaeger

Laboratory Director: Michael Jaeger Date: 10/12/00
Michael Jaeger

QA Approval: Pollyann W Nee Date: 12-Oct-2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE

Determination of Volatile Organics by GC/MS by 8260B using H-P 5972B GC-MS

PRINCIPAL REFERENCES

U.S.EPA Method 8260B, SW-846, 3rd Edition, Update III, December, 1996.

APPLICATION

Water samples with an undiluted concentration range of 1 - 200 μg/L.

SUMMARY of METHOD

This method employs the technique of purge and trap, coupled with a gas chromatograph/mass spectrometer. An aliquot of sample is purged in a gas tight chamber with UHP grade helium to extract the volatile compounds. The vapor is swept onto a sorbent trap where the volatiles are adsorbed. Next, the sorbent trap is heated and back flushed, thereby desorbing the volatiles onto the megabore column within the gas chromatograph. The fused silica capillary column is then temperature programmed to separate the volatiles prior to detection by the mass spectrometer. Table 1 presents the compounds which may be quantitated by this method.

INTERFERENCES

1. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Carryover can be reduced by rinsing the sample syringe between loadings. When an unusually concentrated sample is encountered, it should be followed by the analysis of reagent water as a check of contamination.

2. Samples can be contaminated by the diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. Use a trip blank consisting of reagent water carried through sampling and storage as a check for such contamination.

3. Major contamination sources are volatile materials in the laboratory and purities in the inert purging gas and sorbent trap. Use of UHP quality supply gases along with in-line hydrocarbon and moisture traps will reduce

the potential of contamination. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should investigate to find the source of the contamination and take corrective action to correct it.

4. Improper preservation of samples may lead to biased results. All level 4 samples must be checked after analysis to assure they are preserved to a pH less than 2 with 1:1 hydrochloric acid. Record the measured pH on the cover page of the raw data from the GC-MS data system. If not preserved results must be flagged as approximate data.

TABLE 1

Acetone	cis-1,2-Dichloroethene
Acrylonitrile	trans-1,2-Dichloroethene
Benzene	1,2-Dichloropropane
Bromochloromethane	cis-1,3-Dichloropropene
Bromodichloromethane	trans-1,3-Dichloropropene
Bromoform	Ethyl Benzene
Bromomethane	Hexachlorobutadiene
n-Butanol	2-Hexanone
2-Butanone	Iodomethane
Carbon disulfide	Methylene chloride
Carbon tetrachloride	4-Methyl-2-Pentanone
Chlorobenzene	Naphthalene
Chlorodibromomethane	Styrene
Chloroethane	1,1,1,2-Tetrachloroethane
2-Chloroethylvinylether	1,1,2,2-Tetrachloroethane
Chloroform	Tetrachloroethene
Chloromethane	Toluene
1,2-Dibromo-3-chloropropane	1,2,4-Trichlorobenzene
1,2-Dibromoethane	1,1,1-Trichloroethane
Dibromomethane	1,1,2-Trichloroethane
1,2-Dichlorobenzene	Trichloroethene
1,3-Dichlorobenzene	Trichlorofluoromethane
1,4-Dichlorobenzene	1,2,3-Trichloropropane
Dichlorofluoromethane	Vinyl acetate
1,1-Dichloroethane	Vinyl chloride
1,2-Dichloroethane	o-Xylene
1,1-Dichloroethene	m,p-Xylene

APPARATUS & EQUIPMENT

1. System 1
   - Hewlett Packard Model 5890 Plus gas chromatograph with HP-624 column, 25 m long x 0.20 mm ID
   - Hewlett Packard Model 5972 mass selective detector.
   - Dynatech PTA-30W/S automatic sampler.
   - Tekmar LSC-3000 sample concentrator with 10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001 trap, Supelco 2-4920.
   - Hewlett Packard Kayak XA with MS Chemstation and Enviroquant software package and NBS75K library.
   - Hewlett Packard LaserJet Plus printer.
2. System 2
   - Hewlett Packard Model 5890 Series II chromatograph with DB-624 column, 30 m long x 0.25 mm ID
   - Hewlett Packard Model 5971 mass selective detector.
   - OI 4550 automatic sampler.
   - Tekmar LSC-2000 sample concentrator with 10 cm Carbopack B, 6 cm Carboxen 1000, 1 cm Carboxen 1001 trap, Supelco 2-4920.
   - Hewlett Packard Kayak XA with MS Chemstation and Enviroquant software package and NBS75K library.
   - Hewlett Packard LaserJet Plus printer.
3. Gas tight Syringes, 5 mL Luerlock, Hamilton 1005.
4. Micro syringes:

10 μL, Hamilton 1701	250 μL, Hamilton 1725
25 μL, Hamilton 1702	500 μL, Hamilton 1750
100 μL, Hamilton 1710	1000 μL, Hamilton 1001

5. Volumetric flasks: 10, 50, 100, 500, 1000 mL with ground glass stoppers.
6. Analytical balance, OHAUS Model No. C305-S, 0.1mg sensitivity.
7. Glass scintillation vials, 7 mL and 20 mL with Teflon® -lined screw caps.
8. Pasteur pipets.
9. Mininert valves, Supelco 3-3300M.

CHEMICALS

1. Reagent Water, Milli-Q® or equivalent.
8. Methanol, Purge & Trap grade, Burdick & Jackson 232-1.
3. Purge Gas: He 99.998%
   Carrier Gas: He, 99.998%
4. Assayed individual standard materials:

Acetone	Fluorobenzene
Acrylonitrile	1,2-Dichlorobenzene-d4
2-Butanone	Toluene-d8
2-Hexanone	1,2-Dichloroethane-d4
Carbon Disulfide	4-Bromofluorobenzene
1,4-Dichloro-2-Butene	Methyl tert-butyl ether
4-Methyl-2-Pentanone	Vinyl Acetate

5. Certified standard mixtures:
   •Method 502.2/524.2 mix, Accustandard M-502A-R-10X (2000 µg/mL).
   •Purgeable Organic Matrix Spiking Mixture, AccuStandard Inc. CLP-003-R-10X (2500 µg/mL).
   •Volatile Organic Compounds- Gases, AccuStandard M-502B-10X (2000 µg/mL).

STANDARD PREPARATION

A. Stock Standards

Prepare a stock standard solution for the individual standard materials as follows:

1. Place 6-7 mL methanol in a 10 mL tared volumetric flask. Allow the flask to stand unstoppered until all alcohol-wetted surfaces have dried. Stopper and weigh the flask to the nearest 0.1 mg.
2. For analytes which are liquids at room temperature, add 2 or more drops of the reference standard to the methanol using a 100 µL syringe. Make sure that the material falls directly into the alcohol without contacting the sides of the flask.
3. Quickly stopper the flask and reweigh.
4. Repeat steps A.2. and A.3. for each component to be included in the stock solution. The 100 µL syringe should be rinsed with methanol and the next standard material before the next addition to the flask.
5. When all the stock standard components have been added and individual weights obtained, dilute to volume with methanol, stopper and mix by inverting several times.
6. Store the stock standard solution in a 7 mL amber vial with a PTFE-lined screw cap. Solution is stable for 6 months when stored at 4°C.
7. Calculate the concentration of each component in µg/mL from the net gain in weight.

NOTE: THE WEIGHT OF COMPOUNDS WITH A CERTIFIED PURITY OF 96% OR GREATER CAN BE USED WITHOUT CORRECTION IN CALCULATING THE CONCENTRATION OF THE STOCK STANDARD. Each component concentration should be approximately 10000 µg/mL (will vary with component weight and response).

B. Secondary Calibration Standards (Prepare fresh monthly)

1. From stock standard prepared in Part A of this section:
   a. Place 8 mL methanol into two 10 mL volumetric flasks.
   b. Using appropriate syringes, inject 200 µL of the stock solution into one of the 10 mL volumetric flasks and 1000 µL Volatile Organic Compounds- Gases (VOC's-Gases) into the other volumetric flask.
   c. Dilute to volume with methanol and invert each of the flasks several times to mix.

d. Transfer each solution amber vial equipped with a Mininert valve and label as Secondary Compound Mixture and VOC's- Gases, respectively.

Approximate Component Concentration

Secondary Compound Mixture	200 μg/mL*
VOC's- Gases	200 μg/mL

* Will vary with component weight as determined in Step A.7.

2. From purchased standards:
   a. Place 8 mL methanol into a 10 mL volumetric flask. Transfer 1.0 mL of Method 502.2/524.2 mix to the 10 mL volumetric flask and cap. Dilute to volume with methanol and invert the flask several times to mix. Approximate component concentration: 200 μg/mL.

C. Spiking Solution:
   1. Place 8 mL methanol into a 10 mL volumetric flask.
   2. Using the appropriate syringe, inject 1000 μL Purgeable Organic Matrix Spiking Mixture into the volumetric flask.
   3. Dilute to volume with methanol and invert each of the flasks several times to mix.
   4. Transfer the solution into an amber vial equipped with a Mininert valve and label as Matrix Spike Mixture. Approximate component concentration: 250μg/mL.

D. Internal Standards/Surrogate compounds (IS/Surrogate mix):
   Prepare a stock standard solution for the individual standard materials as follows:
   1. Place 80-90 mL methanol in a 100 mL tared volumetric flask. Allow the flask to stand unstoppered until all alcohol-wetted surfaces have dried. Stopper and weigh the flask to the nearest 0.1 mg.
   2. For analytes which are liquids at room temperature, add approximately 500 μL of the reference standard to the methanol using a 1000 μL syringe. Make sure that the material falls directly into the alcohol without contacting the sides of the flask.
   3. Quickly stopper the flask and reweigh.
   4. Repeat steps A.2. and A.3. for each component to be included in the stock solution. The 1000 μL syringe should be rinsed with methanol and the next standard material before the next addition to the flask.
   5. When all the stock standard components have been added and individual weights obtained, dilute to volume with methanol, stopper and mix by inverting several times.
   6. Store the stock standard solution in a 100 mL volumetric flask. Solution is stable for 1 year when stored at 4°C.

7. Calculate the concentration of each component in μg/mL from the net gain in weight.

NOTE: THE WEIGHT OF COMPOUNDS WITH A CERTIFIED PURITY OF 96% OR GREATER CAN BE USED WITHOUT CORRECTION IN CALCULATING THE CONCENTRATION OF THE STOCK STANDARD. Each component concentration should be approximately 5000 μg/mL (will vary with component density and response).

E. Secondary IS/Surrogate mix (Prepare fresh monthly)
   1. From stock standard prepared in Part D of this section:
      a. Place 50 mL methanol into a 100 mL volumetric flask.
      b. Using a 5 mL pipet, pipet 5.0 mL of the stock solution into the 100 mL volumetric flask.
      c. Dilute to volume with methanol and invert each of the flasks several times to mix.
      d. Solution is stable for 6 months when stored at 4°C.

Approximate Component Concentration

IS/Surrogate Mixture	250 μg/mL*

* Will vary with component weight as determined in Step D.7.

QC CHECK SAMPLE PREPARATION

A. Stock Standards:
   Prepare a stock standard solution for the individual standard materials as follows:
   1. Place 6 - 7 mL methanol in a 10 mL tared volumetric flask. Allow the flask to stand unstoppered until all alcohol-wetted surfaces have dried. Stopper and weigh the flask to the nearest 0.1 mg.
   2. For analytes which are liquids at room temperature, add 2 or more drops of the reference standard to the methanol using a 100 μL syringe. Make sure that the material falls directly into the alcohol without contacting the sides of the flask.
   3. Quickly stopper the flask and reweigh.
   4. Repeat steps A.2. and A.3. for each component to be included in the stock solution. The 100 μL syringe should be rinsed with methanol and the next standard material before the next addition to the flask.
   5. When all the stock standard components have been added and individual weights obtained, dilute to volume with methanol, stopper and mix by inverting several times.
   6. Store the stock standard solution in a 7 mL amber vial with a PTFE-lined screw cap. Solution is stable for at least 4 weeks when stored at 4°C.

7. Calculate the concentration of each component in μg/mL from the net gain in weight.

   NOTE: THE WEIGHT OF COMPOUNDS WITH A CERTIFIED PURITY OF 96% OR GREATER CAN BE USED WITHOUT CORRECTION IN CALCULATING THE CONCENTRATION OF THE STOCK STANDARD. Each component concentration should be be approximately 10000 μg/mL (will vary with component weight).

B. Secondary QC Check Sample (Prepare these solutions fresh monthly).
   1. From prepared stock solutions.
      a. Place 8 mL methanol in two 10 mL volumetric flasks.
      b. Using the appropriate syringes, inject 200 μL of the individual standard material stock solution into one of the 10 mL volumetric flasks and 1000 μL VOC's- Gases into the other volumetric flask.
      c. Dilute to volume with methanol and invert each of the flasks several times to mix.
      d. Transfer each solution to an amber vial equipped with a Mininert valve and label as Secondary Compound Mixture and VOC's-Gases, respectively.

         Approximate Component Concentration

Secondary Compound Mixture	200 μg/mL*
VOC's- Gases	200 μg/mL

         * Will vary with component weight as determined in Step A.7.
   2. Calibration Standards from purchased standards.
      a. Place 8 mL methanol into a 10 mL volumetric flask. Transfer 1.0 mL of Method 502.2/524.2 mix to the 10 mL volumetric flask and cap. Dilute to volume with methanol and invert the flask several times to mix. Approximate component concentration: 200 μg/mL.

PROCEDURE

A. Instrument Conditions:
   System 1
   Environmental Data Analysis conditions:
      Audit trail: on
   GC operating conditions:
      Carrier gas rate: He @ 0.6 mL/min
      Initial temperature: 35°C for 4 minutes
      Temperature program: 8°C/min to 200°C
      Final temperature: 200°C for 5 minutes
      Vacuum compensation: On
      Pressure: 8.7 psi
      Split ratio: 32.7:1
      Injector temperature: 220°C

MS operating conditions:
Mass range: 35-260 amu
Threshold: 50
Scan rate: 1.9 scans/sec
Source temperature: 280°C
Purge & Trap conditions:
Purge temperature: 35°C
Purge flow: 40 mL/min
Sample heater: On
Prepurge time: 0 minutes
Sample preheat time: 1 minute
Sample preheat temperature: 40°C
Purge time: 11 minutes
Dry purge time: 1 minute
Desorb flow rate: 20 mL/min
Desorb preheat temperature: 250°C
Desorb time: 4 minutes
Desorb temperature: 255°C
Bake time: 15 minutes
Bake temperature: 260°C
Bake gas bypass: On
Bake gas bypass delay time: 2 minutes
Autosampler conditions:
Start delay: 0.0 hours
Cycle time: 40 minutes
Last sample:
Last Soil:
Blank last: no
Standard: yes
Sample volume: 5 mL
Dilution: no
Flushes: 2
Stir Time: 0 minutes
Settle time: 0 minutes
Desorb time: 4 minutes

System 2
Environmental Data Analysis conditions:
Audit trail: on
GC operating conditions:
Carrier gas rate: He @ 0.94 mL/min
Initial temperature: 35°C for 3 minutes
Temperature program: 8°C/min to 200°C
Final temperature: 200°C for 3 minutes
Vacuum compensation: On
Split ratio: 35.2:1
Injector temperature: 220°C

MS operating conditions:
Mass range: 35-260 amu
Threshold: 50
Scan rate: 1.9 scans/sec
Source temperature: 280°C

Purge & Trap conditions:
Purge temperature: 35°C
Purge flow: 40 mL/min
Sample Heater: On
Prepurge time: 0 minutes
Sample Preheat temperature: 40°C
Purge time: 11 minutes
Dry purge time: 1 minute
Desorb flow rate: 20 mL/min
Desorb time: 4 minutes
Desorb temperature: 250°C
Bake time: 10 minutes
Bake temperature: 260°C

Autosampler conditions:
Sample Type: Water
First Vial:
Last Vial:
Sample Volume: 5 mL
Dilution Factor: 0
Rinse Volume: 5 mL
Rinses: 2
Standard 1: Yes
Standard 2: No
S. Preheat Stir: No
Stir: No
W. Stir Time: 0 minutes
W. Settle Time: 0 minutes
Syringe Flushes: 2
PreHeat: No
Purge Time: 11 minutes
Desorb Time: 4 minutes
Cycle Timer: 40 minutes
Link to Method: 00

B. Calibration standard preparation:

1. Prepare a series of 7 calibration standards by injecting the volumes of each secondary dilution calibration solution into 100 mL volumetric flasks filled to volume with reagent water.

Level	µL/100 mL	Concentration*
2	1.0	2ppb
5	2.5	5ppb
10	5.0	10ppb
20	10	20ppb
50	25	50ppb
100	50	100ppb
200	100	200ppb

* Will vary with component weight as determined in Step A.7., Standard Preparation

2. Mix by inverting the flasks gently three times.

C. QC Check Sample preparation:
   1. Inject 25 µL of each secondary QC Check Sample Solution into a 100 mL volumetric flask filled to volume with reagent water.
   2. Mix by inverting the flasks gently three times. Approximate component concentration: 50 µg/L*.
      * Will vary with component weight as determined in Step A.7., QC Check Sample Concentrate Preparation.

D. Sample/standard loading (soil preparation see KO5035H, PROCEDURE, Part B. 1.-7. or KO5035L, PROCEDURE, Part 1.-8.):
   1. Fill a 40 mL vial with an aliquot of sample.
   2. Load the vial onto the autosampler tray beginning with position #1. Repeat for all the samples in the batch.

E. Programming the run for samples:
   1. Select WINDOWS file of ENVTop#1. Instrument 1 MS Top window should appear.
   2. Select SEQUENCE, LOAD and file DAILY.s.
   3. Select RUN. Change the Data File Directory to reflect the current date, with the entire directory D:/HPCHEM/1/DATA/MMDDYY.D., where MM, DD and YY represent the current month, day and year. Select OK.
   4. Select EDIT SAMPLE LOG TABLE. The Sample Log Table window will appear. Fields available for editing will include Line, Type, Vial, Data file, Method and Sample Name.
      a. Line refers to the sequential order of the sample log.
      b. Type refers to the type of sample being run (sample, CCV, CCB, Calibration, etc.).
      c. Vial is used to indicate the purge position on the autosampler.
      d. Data file must be a unique name used for the storage of that file.

e. Method refers to stored parameters used for the acquisition, processing and reporting of the sample.
f. Sample name is a descriptor used in the reporting of the sample.

5. After sample log table is completed, select RUN and RUN SEQUENCE. The program will now download the GC, MS and data parameters for the sample on line 1 of the sample log.

F. Initiating a sequence for the purge-and-trap:

1. System 1.
   a. Using the keypad, located on the front of the PTA30/WS, press MANUAL MODE, and PROGRAM SET-UP. Use the arrow key to select AUTO and press PROGRAM SET-UP again. The operating parameters will appear individually each time PROGRAM SET-UP is pressed.
   b. Enter the autosampler conditions specified in A. Instrument Conditions, 1. System 1.
   c. When conditions all entered, return to the screen which reads MAN<<AUTO>> and press AUTO MODE to begin the sampling sequence.
2. System 2.
   a. Using the keypad, located on the front of the OI 4552, press Method, Enter twice edit the Method. The operating parameters will appear individually each time Enter is pressed.
   b. Enter the autosampler conditions specified in A. Instrument Conditions, 2. System 2.
   c. When conditions all entered, press Method twice to return to the main screen. Press Auto, enter the method number and start the autorun.

QUALITATIVE ANALYSIS

A. Target Compounds:

1. Calibrated target compounds may be identified as present if the following criteria are met:
   a. The intensities if characteristic ions of a compound should show symmetry and maximums in the same scan. Excessively noisy chromatograms may interfere with one or more ions in some cases. When that occurs, a library search for that compound must accompany the data submitted for approval and identification listed as suspect, positive or sample reanalyzed with some corrective action to reduce the interferences.
   b. The RRT of the sample component is within $\pm$0.06 RRT units of the RRT of the standard component.
   c. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

d. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different retention times. The height of the valley between the two peaks must be less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

B. Non-Target Compounds:
   1. Tentative identification of uncalibrated compounds may be made if the following criteria are met:
      a. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
      b. The relative intensities of the major ions should agree to within ± 20%.
      c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
      d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
      e. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample because of background contamination or co-eluting peaks.

QUANTITATIVE ANALYSIS

A. When a compound has been qualitatively identified using its primary characteristic ion and its secondary ions (see Table 6), it can be quantified using the integrated abundance of the primary characteristic ion.
   1. All compounds are quantified using the internal standard technique (see CALCULATIONS, section E).
   2. All manual integrations must be initialed and dated by the analyst.
   3. The first order linear regression equation from the initial calibration is used to calculate the concentration in the sample. For reporting Level 4 data samples, if compound concentrations are below the PQL and above the MDL, report the concentration with a "J" qualifier.

CALCULATIONS

A. Relative Response Factor (RRF):

$$RRF = (Ax)(Cis)/(Ais)(Cx)$$

where: Ax = area of compound quantitation ion
Ais = area of IS quantitation ion
Cis = IS concentration
Cx = compound concentration

An average RRF is calculated for each target compound and surrogate from the initial calibration.

B. Percent Relative Standard Deviation:

$$\%RSD = \frac{(\text{standard deviation})}{\text{Average RF}} \times 100$$

where: average RF = average of five initial Response Factors for a compound

C. Percent Difference (%D):

$$\%D = \frac{(\text{average RRFi}) - (\text{RRFc})}{(\text{average RRFi})} \times 100$$

where: average RRFi = average RRF from the initial calibration
RRFc = RRF from the continuing calibration standard

D. Target Compound Concentrations:

$$C_x = \frac{A_x C_{is} DF}{A_{is} RRF}$$

where: C_x = concentration of the compound in the sample
A_x = Area response of the characteristic ion for the compound to be measured.
A_{is} = Area response of the characteristic ion for the internal standard
C_{is} = Concentration of the internal standard.
DF = Dilution factor.

E. Surrogate Percent Recovery:

$$\%\ \text{Recovery} = \frac{(\text{concentration found})}{(\text{concentration spiked})} \times 100$$

F. Matrix Spike Recovery:

$$\%\ \text{Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

where: SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

G. Relative Percent Difference:

$$RSD = \frac{(MSR - MSDR)}{(MSR + MSDR)/2} \times 100$$

where: MSR = matrix spike recovery
MSDR = matrix spike duplicate recovery

H. Adjusted Practical Quantitation Limit (PQL) for Samples:

$$\text{Adjusted PQL} = \frac{(PQL)}{D} \times DF$$

where: D = (100 - %moisture)/100
DF = Dilution Factor

QUALITY CONTROL

A. Initial Calibration

1. The average RF must be calculated and recorded for each compound using the five RF values calculated for each compound from the initial calibration curve. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. These compounds are used to check for compound instability and to check for system instability caused by contaminated lines or active sites in the system. The minimum response factor for SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

2. Using the response factors (RF) generated from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The relative standard deviation should be less than 15% for each compound. However, the RSD for each individual Calibration Check Compound (CCC) must be less than 30%. The CCCs are 1,1-dichloroethane; chloroform; 1,2-dichloropropane; toluene; ethylbenzene; and vinyl chloride. If a RSD of greater than 30% is found for any CCC, corrective action to eliminate the cause must be performed and documented prior to reattempting calibration.

B. Daily Continuing Verification

1. Prior to the analysis of any samples, inject 50 ng of 4-bromoflurobenzene (BFB) to check performance of the MSD. The resultant mass spectra for the BFB must meet all the criteria given in Table 3. These criteria must be demonstrated each 12 hour shift.

TABLE 3

BFB MASS - INTENSITY SPECIFICATIONS (4-Bromofluorobenzene)

Mass	Intensity Required (relative abundance)
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

2. The initial calibration curve for each compound of interest must be checked and verified once every 12 hours by analyzing a calibration standard which is at a concentration near the midpoint concentration for the low level working range of the GC/MS and evaluating the SPCCs and CCCs. The SPCCs must meet the criteria specified in part B.1., Quality Control. If the percent drift for each CCC is less than 20%, the initial calibration is presumed valid. If the criterion is not met (>20% drift) for any one CCC, corrective action must be taken. If no source of the problem can be determined after taking corrective action, a new five point calibration MUST be generated. If the CCCs are not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

3. A method blank must be analyzed and shown to contain less than or equal to the PQL of the target compounds. If a method blank exceeds the limits for contamination, the laboratory shall investigate the source of contamination. Appropriate corrective action shall be taken and documented before further sample analysis occurs.

C. Samples

1. Surrogate (S) recovery limits specified in Table 4 must be met for all blanks, samples, and MS/MSD. **Surrogate recovery limits must be developed semi-annually.**

TABLE 4

SURROGATE RECOVERY LIMITS - Water

Compound	Water % Recovery	Soil % Recovery
Dichloroethane-d4	87-126	80-120
Toluene-d8	87-105	81-117
4-Bromofluorobenzene	95-116	74-121

2. Internal standard (IS) limits must be met for all blanks, samples, and MS/MSD. The IS area for the samples must be between -50 and +100% of the area in the mid-point standard calibration level. The RT shift must be between ± 30 seconds from the RT in the mid-point standard calibration level.
3. A minimum of one spiked sample (MS) and spike duplicate (MSD) must be analyzed per group of 20 or fewer samples. Percent recovery must fall within the acceptance ranges for each analyte specified in Table 5. Matrix spike/matrix spike duplicate acceptance criteria must be developed semi-annually.

TABLE 5

Matrix Spike/Matrix Spike Duplicate Acceptance Criteria

Compound	Water % Recovery	RPD	Soil % Recovery	RPD
1,1-Dichloroethene	78-133	18	66-128	11
Benzene	66-147	19	74-136	12
Trichloroethene	74-121	18	55-118	7
Toluene	81-135	17	58-148	15
Chlorobenzene	85-137	19	72-133	10

4. A laboratory control sample (LCS) can be analyzed per group of 20 or fewer samples to show non-matrix dependant spike recovery. The LCS should be a clean (control) matrix, similar to the sample in weight or volume, spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

TABLE 6

Characteristic Masses (M/Z) for Target Compounds

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion
Fluorobenzene (IS)	96	77
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61,63
Acetone	43	58
Iodomethane	142	127
Carbondisulfide	76	78
Methylene chloride	84	86,49
Acrylonitrile	53	52,51
t-1,2-Dichloroethene	96	61,98
MTBE	73	57
1,1-Dichloroethane	63	65,83
Vinyl acetate	43	86
2,2-Dichloropropane	77	97
cis-1,2-Dichloroethene	96	61,98
MEK (2-Butanone)	43	72
Bromochloromethane	128	130,49
Chloroform	83	85
1,1,1-Trichloroethane	97	99,61
Carbon tetrachloride	117	119
1,1-Dichloropropene	75	110,77
Benzene	78	
1,2-Dichloroethane	62	98
Dichloroethane-d4 (S)	102	
Trichloroethene	95	97,130,132
1,2-Dichloropropane	63	65
Dibromomethane	93	95,174
Bromodichloromethane	83	85,127
2-Chloroethylvinylether	63	65,106
cis-1,3-Dichloropropene	75	77,39
MIBK (4-Methyl-2-pentanone)	43	58,85,100
Toluene d8 (S)	98	
Toluene	92	91
trans-1,3-Dichloropropene	75	77,39
1,1,2-Trichloroethane	83	97,85
2-Bromo-1-chloropropane	77	41

Table 6: Continued

Characteristic Masses (M/Z) for Target Compounds

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion
1,2-Dichlorobenzene d4 (IS)	152	
Tetrachloroethane	164	129,131,165
1,3-Dichloropropane	76	78
Methylbutylketone(2-Butanone)	43	58,57
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109
Chlorobenzene	112	77,114
1,1,1,2-Tetrachloroethane	13	133,119
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78
Bromoform	173	175,254
Isopropyl benzene	105	120
4-Bromofluorobenzene (S)	95	174,176
Bromobenzene	156	77,158
1,1,2,2-Tetrachloroethane	83	85
1,2,3-Trichloropropane	75	77
trans-1,4-Dichloro-2-propene	75	53,88
n-Propyl benzene	91	120
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
tert-Butyl benzene	119	91,134
1,2,4-Trimethylbenzene	105	120
sec-Butyl benzene	105	134
1,3-Dichlorobenzene	146	111,148
4-Isopropyl toluene	119	134,91
1,4-Dichlorobenzene	146	111,148
1,2-Dichlorobenzene	146	111,148
n-Butyl benzene	91	134
1,2-Dibromo-3-chloropropane	155	157
1,2,4-Trichlorobenzene	180	182,145
Hexachlorobutadiene	225	223,227
Napthalene	128	
1,2,3-Trichlorobenzene	180	182,145

TABLE 7

System 1 Retention Times and PQL's for Target Compounds

Compound	Retention Time	PQL (µg/L)
Acetone	3.32	25
Acrylonitrile	4.39	1
Benzene	7.45	1
Bromochloromethane	6.44	1
Bromodichloromethane	9.38	1
Bromoform	14.43	1
Bromomethane	2.10	1
n-Butanol	8.65	25
2-Butanone (MEK)	6.13	5
Carbon disulfide	3.44	25
Carbon tetrachloride	7.11	1
Chlorobenzene	13.00	1
Chloroethane	2.20	1
2-Chloroethylvinylether	9.94	1
Chloroform	6.61	1
Chloromethane	1.65	1
Dibromochloromethane	11.99	1
1,2-Dibromo-3-chloropropane	19.16	1
1,2-Dibromoethane	12.14	1
Dibromomethane	9.07	1
I,2-Dichlorobenzene	17.75	1
1,3-Dichlorobenzene	16.94	1
1,4-Dichlorobenzene	17.10	1
Dichlorofluoromethane	1.47	1
1,1-Dichloroethane	5.07	1
1,2-Dichloroethane	7.50	1
1,1-Dichloroethene	3.18	1
cis-1,2-Dichloroethene	6.05	1
trans-1,2-Dichloroethene	4.38	1
1,2-Dichloropropane	8.89	1
cis,1-3-Dichloropropene	10.12	1
trans-1,3-Dichloropropene	11.07	1
Ethyl Benzene	13.22	1
2-Hexanone (MBK)	11.83	5
Iodomethane	3.37	1
Methylene chloride	3.92	1
4-Methyl-2-Pentanone (MIBK)	10.43	5
Naphthalene	21.09	5
Styrene	14.15	1
1,1,1,2-Tetrachloroethane	13.17	1
1,1,2,2-Tetrachloroethane	15.34	1

TABLE 7: Continued

System 1 Retention Times and PQL's for Target Compounds

Compound	Retention Time	PQL (μg/L)
Tetrachloroethene	11.55	1
Toluene	10.65	1
1,2,4-Trichlorobenzene	20.67	1
1,1,1-Trichloroethane	6.85	1
1,1,2-Trichloroethane	11.36	1
Trichloroethene	8.53	1
Trichlorofluoromethane	2.52	1
1,2,3-Trichloropropane	15.38	1
Vinyl acetate	5.24	1
Vinyl chloride	1.77	1
o-Xylene	14.11	1
m,p-Xylene	13.44	1
Fluorobenzene (IS)	7.80	
1,2-Dichlorobenzene D4 (IS)	17.56	
1,2-Dichloroethane-d4 (S)	7.23	
Toluene-d8 (S)	10.40	
4-Bromofluorobenzene (S)	14.87	

TABLE 8:

System 2 Retention Times and PQL's for Target Compounds

Compound	Retention Time	PQL (μg/L)
Acetone	3.60	25
Acrylonitrile	4.50	1
Benzene	7.30	1
Bromochloromethane	6.34	1
Bromodichloromethane	9.13	1
Bromoform	14.39	1
Bromomethane	2.37	1
n-Butanol	8.34	25
2-Butanone (MEK)	6.07	5
Carbon disulfide	3.74	25
Carbon tetrachloride	6.99	1
Chlorobenzene	12.87	1
Chloroethane	2.49	1
2-Chloroethylvinylether	9.67	1
Chloroform	6.49	1
Chloromethane	1.86	1
Dibromochloromethane	11.80	1
1,2-Dibromo-3-chloropropane	19.50	1
1,2-Dibromoethane	11.98	1
Dibromomethane	8.86	1
1,2-Dichlorobenzene	17.97	1
1,3-Dichlorobenzene	17.09	1
1,4-Dichlorobenzene	17.26	1
Dichlorofluoromethane	1.67	1
1,1-Dichloroethane	5.14	1
1,2-Dichloroethane	7.33	1
1,1-Dichloroethene	3.48	1
cis-1,2-Dichloroethene	6.00	1
trans-1,2-Dichloroethene	4.56	1
1,2-Dichloropropane	8.67	1
cis,1-3-Dichloropropene	9.87	1
trans-1,3-Dichloropropene	10.82	1
Ethyl Benzene	13.10	1
2-Hexanone (MBK)	11.60	5
Iodomethane	3.66	1
Methylene chloride	4.15	1
4-Methyl-2-Pentanone (MIBK)	10.16	5
Naphthalene	21.61	5
Styrene	14.08	1
1,1,1,2-Tetrachloroethane	13.04	1

TABLE 8: Continued

System 2 Retention Times and PQL's for Target Compounds

Compound	Retention Time	PQL(µg/L)
1,1,2,2-Tetrachloroethane	15.31	1
Tetrachloroethene	11.37	1
Toluene	10.44	1
1,2,4-Trichlorobenzene	21.15	1
1,1,1-Trichloroethane	6.74	1
1,1,2-Trichloroethane	11.14	1
Trichloroethene	8.33	1
Trichlorofluoromethane	2.80	1
1,2,3-Trichloropropane	15.37	1
Vinyl acetate	5.27	1
Vinyl chloride	1.98	1
o-Xylene	14.05	1
m,p-Xylene	13.32	1
Fluorobenzene (IS)	7.75	
1,2-Dichlorobenzene D4 (IS)	17.94	
1,2-Dichloroethane-d4 (S)	7.22	
Toluene-d8 (S)	10.32	
4-Bromofluorobenzene (S)	15.01	

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: David Z Bailey Date: 10-11-00
David Bailey

Supervisor: Julie A. Rumsey Date: 10-11-2000
Julie A. Rumsey

Laboratory Director: Michael Jaeger Date: 10/12/00
Michael Jaeger

QA Approval: Pollyann Nee Date: 12 Oct 2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE

Semi-Volatile Compounds by GC/MS
(8270C)

Principal References :

Method 8270C: Test Methods for Evaluating Solid Wastes, Third Edition, Update III, SW-846; U.S. EPA Office of Solid Waste and Emergency Response; Washington, DC., December, 1996.

Method 525.2: Methods for the Determination of Organic Compounds in Drinking Water; U.S. Environmental Monitoring Systems Labs, Cincinnati, OH.

Application :

This method can be used to determine the concentration of various semi-volatile organic compounds (SVOC) in groundwater, TCLP leachates, soils, sediments, waste, and solid sample extracts. The attached quantitation report lists the target compounds, the retention times of the target compounds, the characteristic ions of the target compounds, and the internal standard association of each target compound (see attachment I). Accuracy and precision data, as well as the method detection limit (MDL) for target analytes are listed in Table I.

Summary of Method :

A measured volume or weight of sample is extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0 mL and injected into a GC/MS system. The semi-volatile compounds are separated with a narrow-bore fused-silica capillary column during a temperature-programmed sequence, and are then detected with a mass spectrometer. Qualitative identification of the target compounds in the extract is based on the retention time and the mass spectra determined from standards analyzed on the same GC/MS system under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

Sample collection, preservation and handling:

Matrix	Preservation/ Storage	Container	Sample Holding Time	Extract Hold Time
Aqueous	none; 4°C+/-2°C	1-L amber	7 days	40 days
Soil/sediment	none; 4°C+/-2°C	500mL	14 days	40 days
Waste	none; 4°C+/-2°C	Glass	14 days	40 days
TCLP	none; 4°C+/-2°C	1-L amber	7 days from TCLP leaching procedure	40 days

Store the sample extracts at -10° C, protected from light, in sealed vials (e.g. screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined caps.

Interferences : Method interferences may be caused by contaminants in solvents, reagents or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases or other hydrocarbons that may be extracted from improperly cleaned glassware or extractions vessels. Any non-target interferences present at sufficiently large amounts as to make target analyte quantitation and identification impossible at the reported limit, must be either re-analyzed, cleaned-up or re-extracted until detection is possible.
Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interference. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. If a sample is analyzed containing any target analyte above the linear range, the sample immediately following must not contain those same analytes above the reporting limit. If so, the second sample must be re-analyzed after a clean blank or sample.

Apparatus & Materials : Gas chromatograph - Varian 3400 w/ Leap A2005 autosampler, splitless injector, direct capillary interface
Mass spectrometer - Finnigan Magnum Ion Trap
Capillary column - Restek RTX-5MS, 30m x 0.25mm ID, 0.5μm film thickness

Data system - Compaq Deskpro PC with Finnigan MAT Magnum software
Syringes - 1mL, 2mL, 25µL 10µL, 100µL
10 mL vials with PTFE-lined screw caps
Autosampler vials and crimper, 1.5mL with Teflon crimp caps
Volumetric flasks, class A, 10mL with glass stoppers

Reagents & Standards :

Acetone - pesticide residue grade
Methylene chloride - pesticide residue grade
Stock standards/surrogates and spike solutions - purchased from Supelco or Ultra as certified solution; replace every four months. Replace sooner if comparison with quality control check samples indicates a problem.

Calibration Stock Standards:
TCL Phenols Mix (4-8904) @ 2000µg/mL in methylene chloride
TCL Polynuclear Aromatic Hydrocarbons Mix (4-8905) @ 2000 µg/mL in methylene chloride: benzene (50:50)
TCL Benzidines Mix (4-8906) @ 2000µg/mL in methanol
TCL Hazardous Substance Mix 1 (4-8907) @ 2000µg/mL in methylene chloride
TCL Hazardous Substance Mix 2 (4-8908) @ 2000µg/mL in methylene chloride
TCL Base/Neutrals Mix 1 (4-8900) @ 2000µg/mL in methylene chloride
TCL Base/Neutrals Mix 2 (4-8120) @ 2000µg/mL in methylene chloride
TCL Pesticides Mix (4-8913) @ 2000 µg/mL in toluene:hexane (50:50)

Surrogate Stock Standards:
Semivolatiles Base/Neutrals Surrogate Spike Mix @ 5000 µg/mL in methylene chloride (4-7262)
Semivolatiles Acid Surrogate Spike Mix @ 10,000 µg/mL in methanol (4- 7261)
Semivolatiles Internal Standards Stock Mix @ 2000 µg/mL in methylene chloride (4-8902)
Semivolatiles GC/MS Tuning Stock Standard @ 1000 µg/mL in methylene chloride (GCM-150)

Matrix Spike Stock Standards:
Semivolatiles Base/Neutrals Matrix Spike Mix A @ 1000 µg/mL in methanol (4-8100-U)
Semivolatiles Acid Matrix Spike Mix @ 5000 µg/mL in methanol (4-8878)

Secondary Surrogate Stock Solutions: Using a 2.0 mL syringe add exactly 1.00 mL of Base/Neutral Surrogate Spike Mix to 5mL of acetone in a 10 mL volumetric flask. Dilute to volume with acetone, stopper the flask and invert several times. Repeat this procedure for the Acid Surrogate Spike Mix using 0.50mL of surrogate. This equates to secondary stock concentrations of 500µg/mL.

Surrogate Compounds and Concentrations Table

Surrogate	Primary Stock Conc.	Secondary Stock Conc.
Nitrobenzene-D5	5,000 μg/mL	500 μg/mL
p-Terphenyl-D14	5,000 μg/mL	500 μg/mL
2-Fluorbiphenyl	5,000 μg/mL	500 μg/mL
2-Fluorophenol	10,000 μg/mL	500 μg/mL
Phenol-D5	10,000 μg/mL	500 μg/mL
Tribromophenol	10,000 μg/mL	500 μg/mL

Transfer the stock standard solutions into vials with PTFE-lined screw-caps. Store, protected from light at -10°C or less or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of evaporation or degradation, such as the appearance of anthraquinone from the oxidation of anthracene. Anthraquinone appears as mass 208, and can be seen slightly downfield (10-30 scans) of anthracene (mass 172).

Calibration Standards:
Seven calibration standards are prepared for the initial calibration. The concentrations of these standards are 5μg/mL, 10μg/mL, 20 μg/mL, 30 μg/mL 40 μg/mL, 50 μg/mL and 60 μg/mL, which define the working range of the detector. Each standard is prepared in methylene chloride so that the final volume of each is 1.0 mL. Note: for PAH analyses only, six standards may be prepared and analyzed in order to extend the working range of the instrument. These standards should contain the PAHs and B/N surrogates at concentrations of 5μg/mL, 25μg/mL, 50 μg/mL, 75 μg/mL 1000 μg/mL, and 150 μg/mL.
The following equation is used to determine the volume of a stock standard needed to prepare a given volume of a calibration standard:

$$Vs = \frac{Ccal \times Vcal}{Cs}$$

where

Vs = volume of stock standard required to prepare the calibration standard (mL)
Cs = concentration of the stock standard (μg/mL)
Ccal = concentration of the calibration standard to prepare (μg/mL)
Vcal = volume of calibration standard to prepare (mL)

EXAMPLE:

Prepare 1mL of a 60µg/mL standard from a 2000µg/mL stock standard

$$Vs = \frac{60\mu g/mL \times 1mL}{2000\mu g/mL} = 0.030mL = 30\mu L$$

Calibration Standards Prep Table: amount of each to add to methylene chloride in 1 mL vial

Stock Concentration (µg/mL)	Calibration Standard Concentration (µg/mL)						
	5	10	20	30	40	50	60
TCL Phenols @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
TCL PAH @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
TCL Benzidines @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
TCL HSL 1 @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
TCL B/N 1 @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
TCL B/N 2 @ 2000	2.5 µL	5 µL	10 µL	15 µL	20 µL	25 µL	30 µL
B/N Surr. @ 500	10 µL	20 µL	40 µL	60 µL	80 µL	100 µL	120 µL
Acid Surr. @ 1000	5 µL	10 µL	20 µL	30 µL	40 µL	50 µL	60 µL
Methylene Chloride	970 µL	940 µL	880 µL	820 µL	760 µL	700 µL	640 µL

After the standards are prepared, 20 µL of the 2000 µg/mL Semivolatile Internal Standards stock solution are added to each standard (giving a total volume of 1020 µL for each standard). Prepare fresh calibration standards weekly.

GC/MS tuning standard - A methylene chloride solution containing 50ng/µL of decafluorotriphenyphosphine (DFTPP) should be prepared. The standard will also contain 50ng/µL each of 4,4'-DDT, pentachlorophenol and benzidine to verify injection port inertness and GC column

performance. This is prepared by drawing-up 950 µL of methylene chloride using a 1.0 mL syringe and placing it in a 1.0 mL crimp seal PFTE-lined vial. Using a 100 µL syringe, draw-up 50 µL of the semi-volatiles GC/MS tuning stock standard and add it to the 950 µL of methylene chloride in the vial. Prepare a fresh tuning standard weekly.

Sample Preparation : **The sample extraction procedures are given in the following SOPs:**

Matrix	**SOP Number**	**Extraction Technique**
Aqueous	KO3535	Solid Phase Extraction
Aqueous, TCLP leachates	KO3510	Separatory Funnel
Soils/Sediments	KO3545	Accelerated Solvent Extraction
Wastes	KO3580	Waste Dilution

The sample concentration procedures are given in KO3500B.

Safety : The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated areas.

Material Safety Data Sheets (MSDS) are available to the analyst in each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

Procedure : Instrument Conditions:

Column: Restek RTX-5MS 30m x 0.25mm ID, 0.5µm film thickness

Column flow: Approximately 1mL/min helium

GC Oven temperatures:

Initial column temperature: 40°C for 4 minutes
Column temperature program: 10°C per minute
Final column temperature: 300°C (until at least one minute past the elution time of Benzo(g,h,i)perylene)

GC injector parameters:

Injector temperature: 250°C
Injector: splitless
Injector purge time: 0.8 minutes
Injector liner: 4mm ID quartz or 4mm glass, deactivated
Sample injection volume: 1 µL

Mass Spectrometer and interface parameters:

Mass spectrometer interface: 270°C
Manifold temperature: 220°C
Mass range: 45-450 amu
Scan rate: 500 milli seconds
Emission current: 11 micro amps
A/M amplitude Voltage: 3.5 volts

Tune and Calibration Procedure:
Fifty nanograms of DFTPP must be analyzed at the beginning of each 12 hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a starting GC temperature of 160°C is used to allow for a faster elution of DFTPP. All other instrument conditions must be identical -the mass range, scan rate, and multiplier voltage. Analyze a 1 µL aliquot of the 50ng/µL DFTPP solution. Evaluate the DFTPP peak. The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

The following criteria for acquiring the mass spectrum of DFTPP are required: average the spectrum across at least 3 scans of the peak and background subtract by using a single scan acquired no more than 50 scans prior to the eluting DFTPP peak. The background subtraction should be designed to eliminate column bleed or background ions only. The abundance criteria listed below must be met before standard analysis and subsequent sample analysis can proceed.

NOTE: These criteria have been taken from Method 525.2, Determination of Organic Compounds in Drinking Water By Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry, and represent modern performance criteria that reflect the improved mass spectrometers in use today, such as Ion Traps.

Mass (m/z)	Abundance Criteria
51	10-80% of the base peak
68	<3% of mass 69
69	Exists only
70	<2% of mass 69
127	10-80% of the base peak
197	<2% OF MASS 198
198	Base peak or >50% of mass 442
199	5-9% of mass 198
275	10-60% of the base peak
365	>1% of the base peak
441	Present and less than mass 443
442	Base peak or >50% of mass 198
443	15-24% of mass 442

The following records must be kept for each DFTPP analysis that meets the criteria:

-the date, time, and data file of the analysis
-a spectrum of the scan or enhanced scans
-a tabulation of the ion abundance of the scan or enhanced scans

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA).

Target tune parameters for PFTBA are:

m/z 69:	100%
m/z 70:	1.5-3%
m/z 131:	20-50%
m/z 132:	1.5-3%
m/z 219:	20-60%
m/z 220;	1.5-3%
m/z 414:	present
m/z 464:	present
m/z 502:	> 0.8%

Depending on the nature of the results for the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

Benzidine and pentachlorophenol should be present at their normal responses with minimal peak tailing visible. This is a good check on the system: if pentachlorophenol (a CC) tails badly, and/or has a response below 0.03, the calibration standards should not be analyzed. Perform

injector port and column maintenance and reanalyze the tune/column evaluation standard.

The p,p'-DDT breakdown is calculated using the following equation. The percent breakdown should not exceed 20%

$$\%\text{Breakdown} = \frac{(\text{areaDDE} + \text{areaDDD})}{(\text{areaDDT}+\text{areaDDE}+\text{areaDDD})} \times 100$$

Areas from the total ion chromatogram are evaluated to determine the DDT breakdown.

After the DFTPP criteria have been met, the initial calibration standards are analyzed.

The initial calibration standards consist of seven points, encompassing the linear range of the instrument. The concentrations are: 5 µg/mL, 10µg/mL, 20 µg/mL, 30µg/mL, 40µg/mL, 50µg/mL and 60µg/mL (except for PAH only analysis - conc.= 5 µg/mL, 25µg/mL, 50 µg/mL, 75µg/mL, 100µg/mL, and 150µg/mL.) Set up a sequence and analyze the calibration standards. Be sure to note the standard code ID of each standard in the header line of each standard analyzed. Also, hardcopy the entire sequence table for a file record of analyses performed during each 12 hour shift. The injection volume must be the same for the calibration standards and all sample extracts, i.e. 1µL. Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data. The relative response factor for each compound is calculated using the data system according to the following formula:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion for the compound being measured

Ais= area of the characteristic ion for the internal standard associated with the compound being measured. (See the attached quantitation report for a list of the compounds that are associated with each internal standard.)

Cx = concentration of the compound being measured (µg/mL)

Cis = concentration of the internal standard (40 µg/mL)

The average relative response factor (RRF_{avg}) is calculated for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3 + ... + RRFn}{N}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1} (RRF_i - RRF_{avg})^2}{n-1}}$$

Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards:

$$\%RSD = \frac{SD}{RRF_{avg}} \times 100$$

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of sample extracts can begin.

Calibration Check Compounds - CCC:
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenaphthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a)pyrene

System Performance Check Compounds - SPCC:
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Initial Calibration
CCC: <=30% RSD

SPCC: RRF_{avg}>=0.050

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

The results for all target compounds are evaluated for linearity. If the %RSD is less than or equal to 20%, the calibration is assumed linear through the origin and the average response factor can be used for quantitation. If the %RSD is greater than 20% for any target analytes, a calibration curve using a linear fit should be used for quantitation.

If the correlation coefficient of the linear regression curve is greater than .995, the curve can be used to quantify samples. The analysts must ensure that the curve accurately defines the concentration/response relationship over the entire calibration range.

If CCC and/or SPCC do not meet the stated criteria, all target compounds that are reported must meet the CCC criteria. For example, if naphthalene is the only target to be reported, it can be reported if 1) the CCC and SPCC pass; OR 2) naphthalene passes the CCC criteria (other targets are not evaluated or reported).

Calibration Action Table

Calibration Status	**Action**
CCC/SPCC pass criteria	calibration passes; all targets can be reported
CCC or SPCC fail	calibration fails; any targets that are from the sequence can be reported if the CCC criteria is met for that particular compound

If the initial calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be

aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards.

After the initial calibration criteria (CCC/SPCC) have been met, each target is evaluated for linearity.

- If the %RSD of the target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples.
- If the %RSD of the target compound is greater than 20%, a calibration curve (linear) must be used for the quantitation of samples. A calibration curve may also be used for the compounds that have %RSD less than 20%.

The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured
Cx = concentration of the compound being measured (μg/L)
Cis = concentration of the internal standard (40μg/L)

The initial calibration must be evaluated for the CCC and SPCC criteria even though the calibration curve may be used for quantitation.

Samples are analyzed only after the DFTPP criteria and the calibration acceptance criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the DFTPP and a mid-level calibration standard (usually to 30ng standard).

Analysis Sequence

INITIAL CALIBRATION	CONTINUING CALIBRATION
DFTPP 50ng on column Pentachlorophenol, benzidine, p,p'-DDT added for column evaluation Clock starts at injection	DFTPP 50ng on column Pentachlorophenol, benzidine, p,p'-DDT added for column evaluation Clock starts at injection
Calibration standards	Mid point calibration verification
Samples analyzed until the 12-hour clock expires	Samples analyzed until the 12-hour clock expires

The percent difference or percent drift between the continuing calibration RRF and the average relative response factor (RRF_{avg}) is calculated for each target compound and each surrogate compound:

$$\%difference = \left| \frac{RRF - RRF_{avg}}{RRF_{avg}} \right| \quad x\ 100$$

where
RRF = relative response factor from CCV
RRF_{avg} = average relative response factor from initial calibration curve

$$\%drift = \left| \frac{Ccurve - Ct}{Ct} \right| \quad x\ 100$$

where
Ccurve = concentration from curve(µg/mL)
Ct = true concentration of CCV

The continuing calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The %D (Drift) criteria for CCC and minimum RRF for SPCCs must be met before the analysis of sample extracts can begin.

Continuing Calibration

CCC: <20% difference from initial calibration

SPCC: RRF>= 0.050

If the continuing calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of the injection port lines and assembly. In any case, if the criteria are not met, the analysis of the continuing calibration standard must be repeated. The analyst must be aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards. If the continuing calibration standard repeatedly fails the CCC and SPCC criteria, the initial calibration curve must be reanalyzed and reevaluated.

The initial calibration must be evaluated for the CCC and SPCC criteria even though the calibration curve may be used for quantitation.

Sample Analysis/
Calculations :

Remove the sample extracts to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

Using a 25µL syringe, add 20µL of the internal standard mix (2000ng/µL) to each 1-mL aliquot of the sample extract. The concentration of the internal standard in the extract is 40ng/µL.

Mix the contents of the autosampler vial by inverting several times. Set up a sequence table for the samples and analyze them under the same conditions as the tune and standards.

If a sample is analyzed which contains target compound concentrations above the highest calibration standard (60µg/mL), the sample must be diluted and reanalyzed.

The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100µL of a sample extract is diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100=10). The following table gives some dilution factors:

Dilution Preparation

µL extract-Vext	µL MeCl2	volume of dilution (Vdil-µL)	µL ISTD (2000µg/mL)-Vist	DF
1000	0	1000	20	1
500	500	1000	10	2
200	800	1000	16	5
100	900	1000	18	10
50	950	1000	19	20
20	980	1000	20	50

The concentration of internal standards must remain constant for all extracts and extract dilutions at 40 µg/mL. The following equation can be used to determine the volume of the

2000µg/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vist(\mu L) = 20\mu L - \left(\frac{Vext}{Vdil} x20uL \right)$$

where

Vistd = volume of 2000µg/mL internal standard to add to the diluted extract (µL)
Vext = volume of extract used to prepare the dilution (µL)
Vdil = final volume of the dilution (µL)-1000µL (1.0mL)

Qualitative Analysis for Target Compounds:

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard.

Two criteria must be met in order to positively identify a compound:

1) elution of the sample component within +/- 0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion=100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound makes identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum in order to be considered a positive identification.

Quantitative Analysis for Target Compounds:

Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples.

Aqueous samples - If the average response factor is used, the calculation for samples is:

$$concentration(\mu g/L) = \frac{Ax}{Ais} \times \frac{Cis}{RRF_{avg}} \times \frac{F}{V} \times DF$$

where

Ax	=	area of the characteristic ion of the compound being measured
Ais	=	area of the characteristic ion of the internal standard
Cis	=	concentration of the internal standard (µg/mL)
RRF_{avg}	=	average response factor of the compound being measured
F	=	final volume of extract (mL)
V	=	volume of sample extracted(L)
DF	=	dilution factor

If the linear regression curve is used, the concentration is given:

$$Concentration(\mu g/L) - Curve \times \frac{F}{V} \times DF$$

where

C_{curve}	=	concentration from curve (µg/mL)
F	=	final volume of extract (mL)
V	=	volume of sample extracted (L)
DF	=	dilution factor

The reporting limit (RL) for each sample is given:

$$RL(\mu g/L) = 10 \times \frac{F}{Fqap} \times \frac{V_{qap}}{V} \times DF$$

where

F	=	final volume of extract (mL)
Fqap	=	1.0mL
Vqap	=	1.0L
V	=	volume of sample extracted (L)
DF	=	dilution factor.

NOTE: If V=800mL to 1200mL, assume that Vqap/V = 1 in the calculation of the reporting limit.

Soils:

If the average response factor is used, the calculation for samples is:

$$concentration(\mu g/kg,dw) = \frac{Ax}{Ais} \times \frac{Cis}{RRF_{avg}} \times \frac{F}{(W)(solids)} \times DF$$

where

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (µg/mL)
RRF_{avg} =	average response factor of the compound being measured
F =	final volume of extract (mL)
W =	weight of sample extracted (kg)
solids =	(percent solids)/100
DF =	dilution factor

If the linear regression curve is used, the concentration is given:

$$Conc(\mu g/kg,dw) = Ccurve \times \frac{F}{(W)(solids)} \times DF$$

where

Ccurve =	concentration from curve(µg/mL)
W =	weight of sample extracted (kg)
F =	final volume of extract (mL)
solids =	(percent solids)/100
DF =	dilution factor

Refer to KAR SOP KG462 for details on determining percent solids.

The reporting limit (RL) for each sample is given:

$$RL = 330 \times \frac{F}{Fqap} \times \frac{Wqap}{(W)(solids)} \times DF$$

where

F =	final volume of extract (mL)
W =	weight of sample extracted (kg)
solids =	(percent solids)/100
DF =	dilution factor
F_{qap} =	1.0 mL
W_{qap} =	10.0 g

The concentrations of target compounds in the lab fortified blank and matrix spike samples are determined in the same manner as that of the samples, explained in the preceding paragraphs. These concentrations are then compared to the theoretical spike concentrations and the percent recovery is calculated. The true value for a spiked sample is calculated as follows:

$$concentration = \frac{amounts\ of\ compound\ added}{Volume/weight\ of\ sample\ extracted}$$

For liquid samples, this equation expands to:

$$concentration(\mu g/L) = \frac{Cspike \times Vspike}{Vsample}$$

where
Cspike = concentration of the spiking solution (µg/mL)
Vspike = volume of spiking solution added to the sample (mL)
Vsample = volume of sample spiked (L)

For soil and solid samples, the equation expands to:

$$concentration(\mu g/kg) = \frac{Cspike \times Vspike}{Wsample \times solids}$$

where
Cspike = concentration of the spiking solution (µg/mL)
Vspike = volume of spiking solution added to the sample (mL)
Wsample = weight of sample spiked (kg)
soilds = (percent solids)/100

The percent recovery of the target analytes in the matrix spike sample and lab control samples is calculated:

$$\%recovery(\%REC) = \frac{(Cms - Cs)}{Ts} \times 100$$

where
Cms = concentration of the spiked sample (MS/MSD or LCS/LCSD)
Cs = concentration of the unspiked sample
Ts = theoretical concentration of the spike

The matrix spike sample is analyzed in duplicate (MS/MSD). The relative percent different (%RPD), a measure of precision, is calculated for the MS/MSD pair as follows:

$$\%RPD = \frac{\%REC(MS) - \%REC(MSD)}{(\%REC(MS) + (\%REC(MSD))/2} \times 100$$

The absolute value of the %RPD is evaluated and reported; that is, only positive values are reported. If the MS/MSD cannot be performed, LCS/LCSD are analyzed and evaluated.

QA/QC : The analytical batch consists of up to twenty client samples, prepared by matrix, and a method blank (LMB), matrix spike (MS), matrix spike duplicate (MSD) and a laboratory fortified blank (LFB). A laboratory fortified blank and laboratory fortified blank duplicate may be substituted if insufficient sample is available for MS/MSD.

Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

Initial Demonstration of Capability (IDOC):

Each analyst must demonstrate competence in the analysis of samples by this procedure. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made.

The criteria for this demonstration are the preparation and analysis of four replicate 1.0L aliquots of spiked reagent water, containing the target analytes at approximate 10-50 times their MDL.

To evaluate the performance of the total analytical process, the four spiked samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g. organic-free reagent water for the aqueous matrix and organic-free sand or soil for solid matrix.

The IDOC spike solution itself should contain the analytes of interest at 2-10 µg/mL. Prepare this solution using the same formula for preparing the calibration standard, except the IDOC spike solution should be

prepared in 5.0 mL methanol. To each of the four 1.0L aliquots of reagent water add exactly 1.0 mL of the IDOC spike solution using a 1.0 mL gas tight syringe. Process and analyze the IDOC samples according to the same procedures used to analyze and prepare actual samples.

Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery(s) in µg/L, for each analyte of interest using the four results. Acceptance windows for IDOC analyses are taken from SW-846, Method 8270C. (See Table I.).

MDLs are performed whenever significant changes are made to instrumentation or personnel. Otherwise, MDLs are performed annually by each chemist performing this analysis.

The MS, MSD, and LFB spike analytes are listed in Table II. Recovery windows and % difference limits are taken from SW-846, Tables ONE-39, 40. Surrogate compounds and recovery windows are listed in Table III. Surrogate recovery windows are taken from SW-846, Method 8270, Table 8. Acceptance criteria and corrective actions for all QC items are discussed in Table IV.

Preventative Maintenance :

Routine maintenance of the GC/MS system is critical in order to produce quality data. Assessment of the system and possible maintenance operations to be performed is done daily, based on evaluation of the previous day's samples and the current DFTPP and calibration analyses. All maintenance operations are logged in an Instrument Maintenance Logbook sequentially, per instrument. Typical daily maintenance operations include: changing the injector septum and liner; clipping off 12 inches of the column at the injector end to improve chromatography. Typical routine maintenance operations include: replacing the filament and cleaning the ion source. Scheduled maintenance includes: changing the turbo pump oil every six months; changing the high vacuum pump oil every three months.

Table I: Accuracy, Precision and MDL Data by EPA 3545 (KAR SOP3545)

Compound	Accuracy as recovery, $\bar{x}$ (%)	Precision as Standard Deviation, s	MDL (µg/kg)	Recovery Range %
Phenol	25.09	11.85	37.23	5-112
2-Chlorophenol	51.71	4.582	144.01	23-134
2-Nitrophenol	57.49	25.33	79.63	29-182
2,4-Dimethylphenol	47.00	22.17	69.67	32-119
2,4-Dichlorophenol	65.72	28.79	90.47	39-135
4-Chloro-3-methylphenol	77.30	6.743	21.19	22-147
2,4,6-Trichlorophenol	67.54	46.54	146.27	37-144
2,4-Dinitrophenol	51.88	25.63	80.57	0-191
4-Nitrophenol	63.80	7.165	22.52	0-132
2-Methyl-4,6-dinitrophenol	60.57	44.87	141.03	0-181
Pentachlorophenol	63.84	9.475	29.78	14-176

Table II: MS, MSD, LFB Compounds, Concentrations, and QC Limits.

Mix	Analyte	Concentration Spiked		QC Limits RPD		RECOVERY	
		µg/L	µg/kg	water	soil	water	soil
B/N	1,2,4-Trichlorobenzene	50	5000	28	23	39-98	38-107
B/N	Acenaphthene	50	5000	31	19	46-118	31-137
B/N	2,4-Dinitrotoluene	50	5000	38	47	24-96	28-89
B/N	Pyrene	50	5000	31	36	26-127	35-142
B/N	N-Nitroso-di-n-propylamine	50	5000	38	38	41-116	41-126
B/N	1,4-Dichlorobenzene	50	5000	28	27	36-97	28-104
A	Pentachlorophenol	50	5000	50	47	9-103	17-109
A	Phenol	50	5000	42	35	12-89	26-90
A	2-Chlorophenol	50	5000	40	50	27-123	25-102
A	4-Chloro-3-methylphenol	50	5000	42	33	23-97	26-103
A	4-Nitrophenol	50	5000	50	50	10-80	11-114

Table III: Surrogate Compounds and Recovery Windows by EPA 3545 (KAR SOP 3545)

Mix	Surrogate	QC Limits, % Recovery Soil	Aqueous
B/N	Nitrobenzene-d5	23-120	35-114
B/N	2-Fluorobiphenyl	30-115	43-116
B/N	Terphenyl-d14	18-137	33-141
A	Phenol-d5	24-113	10-94
A	2-Fluorophenol	25-121	21-100
A	2,4,6-Tribromophenol	19-122	10-123

Table IV: QC Items and Corrective Actions

QC Item	Frequency	Acceptance Criteria	Corrective
Tune/Column Evaluation Standard DFTPP 50ng Pentachlorophenol - 50ng Benzidine - 50ng p,p'-DDT 50ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Reanalyze and evaluate -Retune and analyze -Clean source, retune, reanalyze
		Pentachlorophenol and benzidine - present at usual response with no peak tailing visible p,p'-DDT - % breakdown <20%	-Reanalyze -Perform injector port maintenance and reanalyze -Cut more than usual length of column and reanalyze -Replace column
Initial Calibration	After Tune Check and when calibration verification standard fails acceptance criteria. All initial calibration standards.	CCC: %RSD <30% SPCC: RRFavg >0.050 Use cal curve for quantitation if %RSD for any target compound exceeds 15%	-reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standard -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standard
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples	CCC: %Difference <= 20% or %Drift <=20% SPCC: RRF>=0.050	-Reanalyze standard -prepare new standard and reanalyze -Recalibrate
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be 50% to +200% of previous midlevel standard Areas in samples should be evaluated for gross error . Consult superior	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available

Table V (cont): QC Items and Corrective Actions

QC Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >reporting limit	Within Table III limits; one acid/one base may be outside of criteria	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets : <330 µg/kg soils; <5 µg/L waters	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Re-extract entire batch or explain in narrative
Lab Fortified Blank(LFB).	Per Batch	Within the accuracy limits established according to the procedure stated in the QA/QC section	-Evaluate chromatogram, spectra, and integrations -reanalyze extract
Matrix spike (MS) Matrix Spike Duplicate (MSD)	Per batch if sufficient sample volume/weight supplied	Within the control limits established according to the procedure stated in the QA/QC section	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract
Reporting Limit (RL)	Daily (optional)-lowest point on calibration curve if required by client.	Detected at reasonable sensitivity	-Evaluate integrations and spectra; reanalyze -Prepare new standard and reanalyze
Initial Demonstration of Capability (IDOC)	Per analyst	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria

Attachment I: Quantitation Report

Name of Compound	Ref	Quan Masses	R Time	Cal RT	Resp(A)
D4 14-DCbenzene (I.STD	1	150	9:03	9:02	1.000
D8 Naphthalene (I.STD	2	136	12:46	12:46	1.000
D10 Acenaphthene(I.STD	3	164	17:17	17:17	1.000
D10 Phenanthrene(I.STD	4	188	20:02	20:02	1.000
D12 Chrysene (I.STD	5	240	24:38	24:37	1.000
D12 Perylene (I.STD	6	264	28:53	28:53	1.000
D5 Nitrobenzene(S.SURR	2	82	10:47	10:48	0.040
2Fluorobiphenyl(N.SURR	3	172	15:56	15:56	0.517
4-Terphenyl (N.SURR	5	244	22:53	22:54	0.539
n-Nitrosodimethylamine	1	123	1:51	1:51	0.287
N-Nitrosodi-n-propyla!	1	70	10:37	10:37	0.444
n-Nitrosodiphenylamine	4	169	18:40	18:40	0.465
Diphenylamine	4	169	18:40	18:40	0.466
Bis(2-Chloroethyl)eth!	1	93	8:32	8:34	0.142
bis(2-Chloroisopropyl!	1	121	10:11	10:11	0.014
bis(2-Chloroethoxy)me!	2	93	12:27	12:27	0.098
4-Chlorophenylphenyle!	3	204	18:25	18:25	0.836
4-Bromophenylphenylet!	4	248	19:18	19:18	0.117
Phenol	1	94	8:32	8:32	1.406
2-Chlorophenol	1	128	8:34	8:34	0.819
2-Nitrophenol	2	139	11:47	11:47	0.189
2,4-Dimethylphenol	2	122	12:10	12:10	0.281
2,4-Dichlorophenol	2	162	12:31	12:31	0.320
4-Chloro-3-methylphen!	2	107	14:48	14:49	0.384
2,4,6-Trichlorophenol	3	196	15:44	15:43	0.358
2,4-Dinitrophenol	3	184	17:32	17:31	0.132
4-Nitrophenol	3	139	17:45	17:48	0.099
2-Methyl-4,6-dinitrop!	4	198	18:35	18:35	0.138
Pentachlorophenol	4	266	19:51	19:51	0.042
Dimethyl phthalate	3	163	17:01	17:01	1.416
Diethyl phthalate	3	149	18:25	18:25	0.777
Di-n-butyl phthalate	4	149	21:19	21:19	0.841
Butyl benzyl phthalate	5	149	23:51	23:51	1.145
bis(2-Ethylhexyl)phth!	5	149	24:54	24:55	1.857
Di-n-octyl phthalate	5	149	25:54	25:54	2.852
Naphthalene	2	128	12:50	12:50	1.510
Acenaphthylene	3	152	16:57	16:56	1.464
Acenaphthene	3	153	17:21	17:21	1.044
Fluorene	3	166	18:20	18:20	0.809
Phenanthrene	4	178	20:04	20:04	0.971
Anthracene	4	178	20:09	20:09	1.148
Fluoranthene	4	202	22:09	22:09	0.961
Pyrene	5	202	22:31	22:31	2.811
Benzo(a)anthracene	5	228	24:38	24:34	2.869
Chrysene	5	228	24:40	24:41	2.211
Benzo(b)fluoranthene	6	252	26:20	26:19	1.961
Benzo(k)fluoranthene	6	252	26:23	26:24	1.645
Benzo(a)pyrene	6	252	26:48	26:48	1.008
Indeno(1,2,3-cd)pyrene	6	276	28:27	28:26	0.536
Dibenzo(a,h)anthracene	6	278	28:29	28:29	0.337
Benzo(ghi)perylene	6	276	28:51	28:53	0.347
2,4,5-Trichlorophenol	3	196	15:48	15:23	0.295
2-Methylphenol	1	107	10:11	10:40	0.686
2-Fluorophenol (A.SURR	1	112	5:48	5:48	0.980
D5 Phenol (A.SURR	1	99	8:34	8:31	1.135
Tribromophenol (A.SURR	3	332	18:46	18:50	0.186
Nitrobenzene	2	65	10:46	10:50	0.095
Isophorone	2	82	11:31	11:35	0.343
2,4-Dinitrotoluene	3	89	17:49	17:51	0.192
2,6-Dinitrotoluene	3	165	17:04	17:06	0.250
1,3-Dichlorobenzene	*1*	*146*	*8:51*	*8:55*	*1.037*
1,4-Dichlorobenzene	1	146	9:02	9:06	1.063
1,2-Dichlorobenzene	1	146	9:32	9:36	1.037
Hexachloroethane	1	117	10:23	10:28	0.825
1,2,4-Trichlorobenzene	2	180	12:38	12:42	0.378
Hexachlorobutadiene	2	225	13:26	13:31	0.243
Hexachlorocyclopentad!	3	237	15:27	15:30	0.115
2-Chloronaphthalene	3	162	15:59	16:03	1.018
Hexachlorobenzene	4	284	19:27	19:30	0.111
alpha-BHC	4	183	19:20	19:23	0.213
beta-BHC	4	181	19:48	19:49	0.178
gamma-BHC (Lindane)	4	183	19:52	19:56	0.208
delta-BHC	4	183	20:15	20:16	0.169
Heptachlor	4	100	20:57	21:00	0.117
Aldrin	4	66	21:28	21:30	0.092
Heptachlor epoxide	5	353	22:01	22:04	0.108
Endosulfan 1	5	195	22:32	22:35	0.097
4,4'-DDE	5	246	22:49	22:52	0.292
Dieldrin	5	79	22:53	22:57	0.318
Endrin	5	81	23:11	23:14	0.182
Endosulfan II	5	195	23:19	23:21	0.098
4,4'-DDD	5	235	23:23	23:26	0.903
Endrin aldehyde	5	67	24:30	24:33	0.089
Endosulfan sulfate	5	272	23:53	23:55	0.051
4,4'-DDT	5	235	23:53	23:55	0.944
Methoxychlor	5	227	24:38	24:39	1.840
Benzidine	5	184	22:01	22:27	0.017
3,3'-Dichlorobenzidine	5	252	24:36	24:38	0.047
1,2-Diphenylhydrazine(	4	77	18:39	18:43	0.504

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-16-00
Kent Lawrence

Supervisor: _____ Date: 10/17/00
Michael Jaeger

Laboratory Director: _____ Date: 10/17/00
Michael Jaeger

QA Approval: _____ Date: 17 Oct 2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE

Analysis of PCB by EPA Method 8082

1. Principal Reference:

1.1 "Test Methods for Evaluating Solid Waste" - SW-846, 3rd Ed., Update III, U.S.EPA, December 1996.

2. Scope & Application:

2.1 Method 8082 is used to analyze environmental samples and determine the concentration of polychlorinated biphenyls (PCBs) as Aroclors. Open-tubular capillary columns are employed with an electron capture detector (ECD). When compared to packed columns, these fused-silica open-tubular columns offer improved resolution, better selectivity, increased sensitivity and faster analysis. The seven PCB Aroclors listed in Section 2.2 are analyzed using a dual-column analysis system.

2.2

Analyte	CAS Registry No.
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

2.3 PCB Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significantly different peak patterns than those of Aroclor standards.

2.4 Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

2.5 GC/MS Method 8270C is recommended as a confirmation technique when sensitivity permits.

2.6 This method utilizes a dual-column system configuration of two analytical columns joined to a single injection port.

2.7 The analyst must select columns, detectors and calibration procedures most appropriate for the analytes of interest. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Sample chromatograms for all seven PCB Aroclors are provided as attachments to this SOP. GC operating conditions are specified in Section 10.4.

2.8 The reporting limit for each Aroclor in water is 0.10µg/L. The reporting limit in soil is 330µg/kg (on a dry weight basis) for each Aroclor. These reporting limits are highly matrix-dependent and may be elevated when a complex sample type is encountered.

2.9 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method by an initial demonstration of proficiency.

3. Summary of Method:

3.1 A measured volume or weight of sample (approximately 1L for most waters, 2g to 30g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

3.2 Aqueous samples are extracted at neutral pH with methylene chloride using a separatory funnel (refer to KAR SOP KO3510).

3.3 Solid samples are extracted with methylene chloride using pressurized fluid extraction ("accelerated solvent extraction"), according to KAR SOP KO3545.

3.4 Extracts for PCB analysis may be subjected to various cleanup procedures including mercury treatment (Section 10.3.3), florisil cleanup (Section 10.3.4) and sulfuric acid/potassium permanganate cleanup (Section 10.3.5). These cleanup techniques may remove or destroy certain single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.

3.5 Following cleanup, the extract is analyzed by injecting a 2µL aliquot into a gas chromatograph with dual wide-bore fused silica capillary columns and electron capture detectors (GC/ECD).

3.6 The chromatographic data may be used to determine concentrations of each of the nine Aroclors listed in Section 2.2.

4. Interferences:

4.1 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories:

- Contaminated solvents, reagents, or sample processing hardware.
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- Compounds extracted from the sample matrix to which the detector will respond.

4.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination through the analysis of laboratory method blanks and/or reagent blanks. Generally, any phthalates present in a raw sample extract may be removed through the use of sulfuric acid/potassium permanganate cleanup (Section 10.3.5).

4.3 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware, and dry it in an oven at 130°C for several hours, or rinse with methanol

and drain. Store dry glassware (covered) in a clean environment.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, do not dry glassware used from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

4.4 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur is generally removed by using mercury cleanup (Section 10.3.3).

3. Apparatus & Equipment:

5.1 Tremetrics 9001 GC with dual Electron Capture Detectors, Leap Technologies CTE-A200SE Autosampler and ChromPerfect data system with PCB Calculator software.
GC columns: J&W Scientific DB-5 (30m x 0.53mm ID, 1.5µm film thickness) and J&W Scientific DB-35 (30m x 0.53mm ID, 1.0µm film thickness).
Column rinsing kit: Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000) or equivalent.
Volumetric flasks, Class A, 10mL and 25mL, for preparation of standards.
Syringes, Hamilton, 700 series and gas-tight - 10µL, 25µL, 100µL, 250µL, 500µL, 1.25mL and 2mL.
Borosilicate glass vials, 20mL.
Vials, amber, screw cap, 40mL.
Vials, glass with polytetrafluoroethylene(PTFE)-lined screw caps or crimp tops, 1 and 20mL.
Syringe, 10cc disposable.
Aluminum weighing boat.
Vortex mixer.
Turbovap concentrating tubes and rack.
Pasteur Pipets, 6" disposable.
Florisil Cartidges, Waters Sep-Pak Plus, Grade "A" (Waters Part No. WAT020525).
Disposable pipet, graduated, 5mL.
Pipet bulbs.
Teflon squeeze bottle, 500mL.
Graduated cylinder, glass, 500mL.
Griffin beaker, glass, 1000mL.
Erlenmeyer Flask, glass, 1000mL.
Glass jug, amber, 4L.

4. Sample Handling:

6.1 PCBs in Water: Store in a glass container with Teflon-lined cap at 4°C. Holding times are 7 days until extraction and 40 days for analysis of extract stored in sample freezer.

6.2 PCBs in Soil: Store in a glass container with Teflon-lined cap at 4°C. Holding times are 14 days until extraction and 40 days for analysis of extract stored in sample freezer.

5. Reagents:

7.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 NOTE: Store the standard solutions (stock, composite, calibration, internal and surrogate standards) at 4°C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. All stock standard solutions must be replaced within one year; replace standards sooner if routine QC indicates a problem. All other standard solutions must be replaced within six months, or earlier if routine QC indicates a problem.

7.3 Sample extracts prepared by Methods 3510, 3520, 3545 or 3550 need to undergo a solvent exchange step prior to analysis. The following solvents are necessary for solvent exchange and/or dilution of sample extracts. All solvents should be pesticide quality or equivalent and should be determined to be phthalate-free through the analysis of laboratory method blanks and/or reagent blanks.

n-Hexane, C_6H_{14}.
Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$.

7.4 The following solvents may be required for the preparation of standards. All solvent lots must be pesticide quality or equivalent and should be determined to be phthalate-free through the analysis of laboratory method blanks and/or reagent blanks.

Acetone, $(CH_3)_2CO$.
Toluene, $C_6H_5CH_3$.
Organic-free reagent water.

7.5 The following reagents and materials may be required for sample extraction or cleanup:

Sulfuric acid, H_2SO_4, concentrated, ACS grade.
Potassium permanganate, $KMnO_4$, crystals, ACS grade.
Mercury, triple-distilled.
Hexane, C_6H_{14} - Pesticide quality or equivalent.

Sulfuric acid/water, H_2SO_4/H_2O (1:1, v/v):
Slowly add, from a 500mL glass graduated cylinder, 250mL of concentrated H_2SO_4 to 250mL organic-free reagent water in a 1000mL glass beaker. Caution! The reaction will generate a significant amount of heat.

Potassium permanganate, $KMnO_4$ (5 percent aqueous solution, w/v):
Weigh 50g of $KMnO_4$ into an aluminum weighing boat and add to 1000mL of organic-free reagent grade water in a 1000 mL Erlenmeyer flask. Using a magnetic stir bar and stir plate, mix until the $KMnO_4$ is dissolved. Store in a 4L amber glass jug.

Florisil Cartridges, Waters Sep-Pak Plus, Grade "A" (Waters Part No. WAT020525).

6. Preparation of Standards:

8.1 Stock standard solutions

Aroclor 1016 (Supelco, Cat.No. 4-8097), 1000µg/mL in isooctane
Aroclor 1221 (Supelco, Cat.No. 4-8098), 1000µg/mL in isooctane
Aroclor 1232 (Supelco, Cat.No. 4-4805), 1000µg/mL in isooctane
Aroclor 1242 (Supelco, Cat.No. 4-4806), 1000µg/mL in isooctane
Aroclor 1248 (Supelco, Cat.No. 4-4807), 1000µg/mL in isooctane
Aroclor 1254 (Supelco, Cat.No. 4-4808), 1000µg/mL in isooctane
Aroclor 1260 (Supelco, Cat.No. 4-4809), 1000µg/mL in isooctane

8.2 Surrogate standard solution: Pesticide Surrogate Spike Mix (Supelco, Cat.No. 4-8460)
200µg/mL each component in acetone:
Decachlorobiphenyl
Tetrachloro-m-xylene

8.3 Intermediate stock solutions

8.3.1 Aroclor 1016/1260 Mix (10µg/mL each in hexane). Dilute 0.100mL of each 1000µg/mL stock standard to 10mL with hexane using 250µL Hamilton syringe and 10mL class A volumetric flask. Store in 20mL glass vial with PTFE-lined screw cap and place in the standards freezer.

8.3.2 Aroclor 1221, 1232, 1242, 1248 and 1254 (individual) stock solutions (10µg/mL in hexane). Dilute 0.100mL of 1000µg/mL stock standard to 10mL with hexane using a 250µL Hamilton syringe and 10mL class A volumetric flask. Store all individual solutions in 20mL glass vials with PTFE-lined screw caps and place in the standards freezer.

8.3.3 Surrogate standard (20µg/mL each in hexane). Dilute 1.00mL of 200µg/mL stock surrogate mix to 10mL with hexane using a 1.25mL Hamilton syringe and 10mL class A volumetric flask. Store in 20mL glass vial with PTFE-lined screw cap and place in the standards freezer.

8.4 Surrogate spiking solutions

8.4.1 To prepare aqueous surrogate spiking solution (2µg/mL each in acetone): Dilute 0.250mL of 200µg/mL surrogate spike mix to 25mL with acetone using a 500µL Hamilton syringe and 25mL class A volumetric flask. Using a 250µL syringe, add 100µL of aqueous surrogate spiking solution to 1L of sample to create a 0.20µg/L spike. Store the aqueous surrogate spiking solution in a 40mL amber glass vial with a PTFE-lined screw cap and place in the standards freezer.

8.4.2 To prepare soil surrogate spiking solution (20µg/mL in acetone): Dilute 1.00mL of 200µg/mL surrogate spike mix to 10mL with acetone using a 1.25mL Hamilton syringe and 10mL class A volumetric flask. Using a 250µL syringe, add 100µL of soil surrogate spiking solution to 10g of sample to create a 200µg/kg spike. Store the soil surrogate spiking solution in a 20mL glass vial with a PTFE-lined screw cap and place in the standards freezer.

8.5 PCB (Aroclor) working solutions

8.5.1 Aroclor 1016/1260 mix calibration standards (0.10, 0.50, 1.00, 2.00 and 3.00µg/mL). Add 0.10, 0.50, 1.00, 2.00 and 3.00mL respectively of the 10µg/mL Aroclor 1016/1260 mixture to each of five 10mL class A volumetric flasks. Dilute each solution to 10mL with hexane. The surrogates are then added to the Aroclor 1016/1260 0.50µg/mL working standard at 0.50µg/mL each. This is accomplished by adding 0.250mL of the 20µg/mL intermediate surrogate solution using a 500µL Hamilton syringe, during the preparation of the Aroclor 1016/1260 0.50µg/mL working solution.

NOTE: Each of the five Aroclor 1016/1260 working solutions are used for initial calibration. The maximum acceptable relative standard deviation for the five-point initial calibration is 20 percent. The Aroclor 1016/1260 0.50µg/mL working standard is also used for continuing calibration. See Section 10.8.3 for the acceptance criterion related to continuing calibration verification.

8.5.2 Aroclors 1221, 1232, 1242, 1248 and 1254 (individual) working solutions (0.50µg/mL each). Add 0.50mL of the 10µg/mL intermediate stock and dilute to 10mL with hexane using a 1000µL Hamilton syringe and a 10mL class A volumetric flask. The surrogates are then added to each individual Aroclor 0.50µg/mL working standard at 0.50µg/mL each. This is accomplished by adding 0.250mL of the 20µg/mL intermediate surrogate solution using a 500µL Hamilton syringe, during the preparation of each individual Aroclor 0.50µg/mL working solution.

NOTE: In addition to the five Aroclor 1016/1260 calibration standards, each of the (individual Aroclor) 0.50µg/mL working solutions is analyzed at the time of initial calibration. Because only a single-point calibration is performed for each of these other Aroclors, no RSD performance criterion is applied.

8.6 Quality control check (secondary source) standards and spiking solutions

8.6.1 Aroclor 1221 (Restek Cat. No. 32007), 1000µg/mL in hexane
Aroclor 1232 (Restek Cat. No. 32008), 1000µg/mL in hexane
Aroclor 1242 (Restek Cat. No. 32009), 1000µg/mL in hexane
Aroclor 1248 (Restek Cat. No. 32010), 1000µg/mL in hexane
Aroclor 1254 (Restek Cat. No. 32011), 1000µg/mL in hexane
Aroclor 1016/1260 (Restek Cat. No. 32039), 1000µg/mL in hexane

8.6.2 All Aroclor quality control check standards are prepared at 0.50µg/mL in hexane. The Aroclor 1016/1260 QC check standard is analyzed with the continuing calibration standard every 12-hour shift. This additional quality control measure serves to confirm the accuracy of the Aroclor calibration standards. The results for both standards must satisfy the acceptance criterion for continuing calibration verification (see Sections 10.8.3 and 10.8.4). Consult Sections 8.3 and 8.5 for information regarding the preparation of 0.50µg/mL standards.

8.7 Quality control check (secondary source) surrogate standards and spiking solutions

8.7.1 Pesticide surrogate mix (Restek Cat. No. 32000), 200µg/mL each in acetone:
Decachlorobiphenyl
2,4,5,6-tetrachloro-m-xylene

8.7.2 The QC surrogates are added to the Aroclor 1016/1260 0.50µg/mL QC check standard and each individual Aroclor 0.50µg/mL QC check standard at 0.50µg/mL each. Consult Sections 8.3 and 8.5 for information regarding the preparation of 0.50µg/mL standards.

8.8 PCB (Aroclor) spiking solution (prepared from QC check standards)

8.8.1 Aqueous PCB spiking solutions (5µg/mL each Aroclor 1016/1260 and Aroclor 1242). Dilute 0.125mL of 1000µg/mL Aroclor stock solution to 25mL with hexane using a 250µL syringe and 25mL class A volumetric flask. Transfer the aqueous PCB spiking solution to a 40mL amber vial and store in the standards freezer.

8.8.2 Using a 200µL syringe, add 100µL of 5µg/mL aqueous PCB spiking solution to 1L of sample to create a 0.50µg/L spike.

8.8.3 Soil PCB spiking solutions (25µg/mL each Aroclor 1016/1260 and Aroclor 1242). Dilute 0.625mL of 1000µg/mL Aroclor stock solution to 25mL with hexane using a 1000µL syringe and 25mL class A volumetric flask. Transfer the soil PCB spiking solution to a 40mL amber vial and store in the standards freezer.

8.8.4 Using a 1.0mL syringe, add 0.500mL of 25µg/mL soil PCB spiking solution to 10g of sample to create a 1250µg/kg spike.

8.9 Calibration standards for PCB Aroclors

8.9.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five PCB Aroclors. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations is sufficient to demonstrate the linearity of the detector response without the need to perform initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentration of Aroclor 1016 or Aroclor 1260 present in a sample.

8.9.2 According to the instructions in Section 8.5.1, prepare five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with hexane. These concentrations correspond to the expected range of concentrations generally found in actual samples and bracket the linear range of the detector.

8.9.3 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described above have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor. Prepare a (0.50µg/mL) standard for each of the other Aroclors following the instructions in Section 8.5.2. This concentration corresponds to the approximate midpoint of the linear range of the detector.

9. Safety:

9.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. A lab coat, gloves and safety glasses or a face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution must be performed in a hood.

9.2 Material Safety Data Sheets (MSDS) are available to all laboratory employees. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

10. Procedure:

10.1 Sample extraction

10.1.1 Refer to the following KAR SOPs for the appropriate matrix and extraction technique:

Aqueous	O3535: Solid Phase Extraction
Aqueous, TCLP Extracts	KO3510: Separatory Funnel
Soils/Sediments	KO3545: Accelerated Solvent Extraction
Wastes	KO3580: Waste dilution

10.2 Extract concentration

10.2.1 Refer to KAR SOP KO3500B.

10.3 Extract cleanup

10.3.1 Reference Methods: EPA 3660A Sulfur Cleanup, EPA 3620B Florisil Cleanup, and EPA 3665A Sulfuric Acid/Permanganate Cleanup.

NOTE: KAR is aware that Method 3660A has been updated and that Method 3660B (SW-846, Revision 2, December 1996) no longer includes a mercury cleanup option for sulfur removal. Based on our experience, however, mercury cleanup is vastly superior to the two remaining sulfur removal options in 3660B (copper and TBA sulfite cleanup). We believe that the mercury cleanup option was likely removed from Method 3660B due to safety (toxicity) concerns. However, we also believe that experienced chemists may reasonably be expected to use (and dispose of) mercury responsibly. Therefore, we continue to perform mercury cleanup for the removal of sulfur from organic extracts intended for PCB analysis.

10.3.2 Summary: All PCB extracts are cleaned up using mercury and florisil before analysis. Mercury is added to the sample extract in an autosampler vial, capped, and shaken for 30 minutes. Next, a florisil cleanup is performed by flushing the mercury-treated extract through a Waters florisil Sep-Pak Plus cartridge. The extract is then reconcentrated to the original pre-treated volume. Following initial analysis of the extract, the analyst must determine if an additional mercury cleanup is necessary. If major interferences still exist, the more rigorous sulfuric acid/ permanganate cleanup is then performed.

10.3.3 Removal of sulfur using mercury

10.3.3.1 Caution: Mercury is a highly toxic metal. All operations involving mercury should be performed in a hood. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

10.3.3.2 Concentrate the sample extract to exactly 1.0mL or other known volume.

10.3.3.3 Pipet 1.0mL of the extract into a clean glass autosampler vial using the 1.25mL Hamilton syringe. Using a 6" disposable Pasteur pipet, add one to three drops of mercury to the vial.

10.3.3.4 Seal the vial, place it on the vortex shaker and agitate the contents of the vial for 30min.

10.3.3.5 Store the sample extracts with mercury at 4°C until florisil cleanup may be performed.

10.3.4 Florisil cleanup

10.3.4.1 Connect the florisil cartridge onto the "luer lok" end of the 10cc disposable syringe and remove the syringe plunger.

10.3.4.2 Transfer 10mL of hexane to the syringe, using the Teflon squeeze bottle. Return the plunger to the syringe and begin to force the hexane through the florisil cartridge and into a waste beaker. Stop short of inserting the plunger fully inside the syringe body. Stop when approximately 0.5mL of hexane remains in the syringe. Take great care to prevent the cartridge from going dry at this point, as channeling through the florisil could result.

10.3.4.3 Place the syringe and cartridge on top of a clean solvent-rinsed Turbovap concentrating tube. The tip of the cartridge should rest against the inside of the tube.

10.3.4.4 DO NOT allow the cartridge to go dry. If necessary, more hexane may be added with the Teflon squeeze bottle. The mercury-treated extract is now transferred into the syringe barrel with a 6" disposable Pasteur pipet. To complete the transfer, rinse the autosampler vial twice more with small volumes of hexane from the Teflon squeeze bottle. Using the syringe plunger, push sample through the cartridge into the concentrating tube until approximately 0.5mL of sample extract remains in the syringe. Now add 10mL of hexane and slowly push this entire volume of solvent through the Sep-Pak into the concentrating tube. This completes the florisil cleanup. After the extract is reconcentrated via Turbovap (KAR SOP KO3500B) to its original pre-treated volume, it is ready for analysis.

10.3.5 Sulfuric acid/potassium permanganate cleanup

10.3.5.1 Add 5mL of (1+1) H_2SO_4/H_2O to a clean 20mL vial using a 5mL disposable pipet and pipet bulb. Transfer the sample extract to the vial with a 6" disposable Pasteur pipet. To complete the transfer, rinse the extract vial two times with small volumes of hexane from the Teflon squeeze bottle. Add additional hexane to the vial until the total volume reaches 4mL.

10.3.5.2 Cap the vial with a Teflon-lined screw cap and proceed to shake vigorously for one minute. Set the vial aside and let the two phases separate. When separated, use a 6" Pasteur pipet to transfer the (top) hexane layer to a clean 20mL vial. Add a second 4mL aliquot of hexane from the Teflon squeeze bottle to the acid vial, then cap it and shake for another minute. Let the two phases separate once more and again transfer the hexane layer to the second vial using a Pasteur pipet. This completes the acid portion of the cleanup.

10.3.5.3 Using a 5mL disposable pipet, add 5mL of $KMnO_4$ (5% aqueous solution, w/v) to the acid-cleaned extract. Cap the sample vial and shake for 1 minute. Allow the two phases to separate. When separated, use a 6" Pasteur pipet to transfer the (top) hexane layer to a clean 20mL vial. Add a second 4mL aliquot of hexane from the Teflon squeeze bottle to the $KMnO_4$ vial, then cap it and shake for another minute. Let the two phases separate once more and again transfer the hexane layer to the second vial to combine the extracts.

10.3.5.4 The $H_2SO_4/KMnO_4$-treated extract is now taken through the florisil cleanup process (described in Section 10.3.4) once more. After the extract is reconcentrated via Turbovap (KAR SOP KO3500B) to its original pre-treated volume, it is ready for analysis.

10.4 GC operating conditions:

Column 1: DB-5 (30m x 0.53mm ID, 1.5µm film thickness)
Column 2: DB-35 (30m x 0.53mm ID, 1.0µm film thickness)
Guard column: (J&W) 10m x 0.53mm ID, deactivated fused silica
Carrier gas (Helium) flow rate: 6mL/min
Makeup gas (Nitrogen) flow rate: 39mL/min
Temperature program:
a) 0.5min hold at 150°C
b) 150°C to 190°C, at 12°C/min
c) 2.0min hold at 190°C
d) 190°C to 275°C, at 4°C/min
e) 10.0min hold at 275°C
f) 37.08min total run time
Injector temperature: 240°C
Detector temperature: 350°C
Injection volume: 2µL
Solvent: Hexane
Type of injector: Flash vaporization
Detector type: Dual ECD
Range: 10 volts
Type of splitter: Restek Universal Y-shaped Press-Tight connector

10.5 Calibration

10.5.1 As noted above, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five PCB Aroclors. Therefore, this standard will be used to establish the linearity of the detector and to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard will also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. A five-point initial calibration will be performed using the mixture of Aroclors 1016 and 1260.

Standards of the other five Aroclors are necessary for pattern recognition. These standards will also be used to determine a single-point calibration factor for each Aroclor. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards.

In situations where only a few Aroclors are of interest for a specific project, a five-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern) may be employed in place of the 1016/1260 mixture described or the pattern recognition standards described above.

10.5.2 Initial calibration of the system: Inject 2µL of the 0.50µg/mL individual Aroclor working solutions in addition to the 0.10, 0.50, 1.00, 2.00 and 3.00µg/mL working solutions of the Aroclor 1016/1260 mixture.

10.5.3 Using the PCB Calculator program, calibrate each Aroclor by "tagging" as many as seven of the most prominent peaks for that particular Aroclor and calculating a calibration factor (according to the formula in Section 10.6.6) based on one-point external standard calibration.

NOTE: The five standard levels analyzed for Aroclor 1016 and Aroclor 1260 are used to prove linearity and demonstrate that the detectors are not saturated by the standard of highest concentration. During sample analysis, any extract that produces individual PCB peak areas greater than those in the highest Aroclor 1016/1260 standard must be diluted and reanalyzed until a response that falls within the linear dynamic range (0.10µg/mL to 3.00µg/mL) is obtained.

Aroclor 1016 and 1260 concentrations are calculated using the calibration factor generated from the most recent continuing calibration. Concentrations of the other Aroclors are calculated using the calibration factor established for that Aroclor at the time of initial calibration. At any time, the analyst may choose to run an appropriate (individual Aroclor) standard to confirm retention times of the Aroclor peaks on both GC analytical columns. However, this does not constitute an attempt at continuing calibration verification; therefore, no RSD criterion need be considered.

10.6 Quantitation of PCBs as Aroclors

10.6.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

10.6.2 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks for Aroclors 1221, 1232, 1242, 1248 and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

10.6.3 Once the Aroclor pattern has been identified, compare the responses of three to seven major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the peaks selected should include at least one peak that is unique to that Aroclor. A concentration is determined for each of the characteristic peaks using the appropriate individual calibration factor and the equation in Section 10.6.9.1 (water samples) or 10.6.9.2 (soil samples). The resultant (three to seven) peak concentrations are averaged to determine the concentration of the associated Aroclor. Seven peaks are used for the Aroclor 1016/1260 mixture, none of which are common to both of these Aroclors.

10.6.4 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 1 lists thirteen specific PCB congeners found in Aroclor mixtures.

10.6.5 Record the peak area (or height) for each characteristic Aroclor peak to be used for quantitation.

NOTE: Peak area measurements are typically employed for PCB calculations. However, at the analyst's discretion, peak height may be substituted when overlapping peaks make the integration of peak areas difficult. In any case, the use of either peak area or height must remain consistent for an entire batch of standards and samples.

10.6.6 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the following equation:

$$CF = \frac{\text{Peak area (or height) in the standard}}{\text{Total mass of the standard injected (in nanograms)}}$$

10.6.7 Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the seven peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least three (and as many as seven) calibration factors, one for each selected peak. An Aroclor calibration factor is calculated by averaging all associated peak calibration factors.

10.6.8 The five Aroclor 1016/1260 calibration factors generated during the initial multipoint calibration are used to establish the linear dynamic range of the analytical system. The GC data system calculates the average calibration factor, the associated standard deviation, and the relative standard deviation (RSD) for each Aroclor (1016 and 1260) in the initial calibration mix. If the RSD for each of these two Aroclors does not exceed 20 percent, linearity is assumed and the average calibration factor is employed for calculations performed within the initial 12-hour analytical period. After 12 hours have elapsed, a continuing calibration standard must be

analyzed. If the continuing calibration verification acceptance criterion is satisfied (per Section 10.8.3) for both Aroclors, the calibration factors from the continuing calibration standard are used for subsequent calculations (until the current 12-hour period ends and the continuing calibration verification process must be repeated). Therefore, Aroclor 1016 and 1260 concentrations are essentially calculated using the calibration factor generated from the most recent continuing calibration. Concentrations of the other Aroclors are calculated using the calibration factor established for that Aroclor at the time of initial calibration. Because only a single-point initial calibrations is performed for Aroclors other than 1016 and 1260, no acceptance criteria exist for these other Aroclors.

10.6.9 Calculation of sample results

The concentration of each analyte in the sample is determined by comparing the detector response (peak area or height) to the response for that analyte in the initial or continuing calibration. The concentration of an analyte may be calculated as follows, depending on the sample matrix:

10.6.9.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area per ng).

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same.

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

10.6.9.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_s, V_t, D, $\overline{CF}$, and V_i are as described in 10.6.9.1, and

W_s = Weight of sample extracted (g). Although this term is generally expressed as dry weight, either the wet weight or dry weight may be used, depending upon the specific application of the data. When dry weight reporting is desired, W_s is equivalent to the wet weight of extracted sample multiplied by the percent solids (expressed as a decimal): $W_s = W_{wet} \times$ (% solids/100). Refer to KAR SOP KG462 for details regarding percent solids determination.

Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

10.6.10 Quantitation notes:

Use only peaks appearing in both the standard and the sample for calculations.

Round the calculated concentration to two significant figures except when the results are less than ten times the reporting limit. If this occurs, report only one significant figure.

The reporting limit in the absence of interferences will be 0.1µg/L for water samples and 330µg/kg (on a dry weight basis) for soils. Identify any Aroclor detected on the analytical report.

10.6.11 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. In such instances, if results in terms of Aroclors are absolutely required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

10.6.12 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection by GC/MS.

10.6.13 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1ng/µL.

10.6.14 The GC/MS must be calibrated for the specific target analytes. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

10.6.15 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

10.6.16 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere. However, if PCBs are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

10.7 Retention time windows

10.7.1 Absolute retention times will be used for the identification of Aroclor peaks. A retention time window study must be performed whenever new column(s) are installed or whenever significant changes and/or major maintenance are performed on the gas chromatographs. This study consists of 3 standard injections over a 72 hour period and calculation the retention time window of all surrogates, and major constituents of multi-component analytes (PCBs) as ± 3 times the standard deviation of the mean absolute retention time established over the 72 hour period. These windows must be calculated, documented , and readily accessible for easy reference.

10.7.2 Monitor retention time stability by comparing the absolute retention times of analyte peaks in both initial and continuing calibration standards. Acceptance criteria are expressed as the maximum acceptable retention time shift, in minutes. A warning limit of ±0.10 minutes retention time shift has been established for PCB analysis at KAR Laboratories. If the retention times vary by more than the windows established according to the procedure in sec. 10.7.1, then a new set of calibration standards must be analyzed and the system must be recalibrated.

10.7.3 For Aroclors other than 1016 or 1260, the analyst may wish to analyze the appropriate (individual Aroclor) standard following an apparent positive sample result. If so, the chromatographic pattern and major peak retention time data from both analytical GC columns may be used to aid Aroclor identification and confirmation.

10.8 Gas chromatographic analysis of sample extracts

10.8.1 Identical GC operating conditions must be employed for both instrument calibration and the analysis of samples.

10.8.2 Verify calibration each 12-hour shift by injecting the (0.50µg/mL Aroclor 1016/1260 mix) continuing calibration standard prior to conducting any sample analyses. The (0.50µg/mL Aroclor 1016/1260 mix) QC check standard is analyzed with the continuing calibration standard every 12-hour shift.

A continuing calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring reinjection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the continuing calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

10.8.3 The calibration factor for each analyte calculated from the continuing calibration standard (CF_c) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{(CF_{mean} - CF_c)}{CF_{mean}} \times 100$$

10.8.4 Similarly, the calibration factor for each analyte calculated from the QC check standard (CF_{QC}) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{(CF_{mean} - CF_{QC})}{CF_{mean}} \times 100$$

10.8.5 If the 15 percent criterion is exceeded for any (continuing calibration standard or QC check standard) calibration factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

10.8.6 If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed.

10.8.7 Inject a 2µL aliquot of the concentrated sample extract. Record the volume injected to the nearest 0.05µL and the resulting peak size in area (or peak height) units.

10.8.8 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Section 10.9.

10.8.9 Quantitative results are determined for each identified Aroclor using the procedures described in Section 10.6.9. If the responses in the sample chromatogram exceed the calibration range of the

system, dilute the extract and reanalyze. The use of peak height rather than peak area in quantitation is recommended when overlapping peaks cause errors in area integration.

10.8.10 Each sample analysis must be bracketed with an acceptable initial calibration, QC check standard and continuing calibration standard(s) (each 12-hour shift) or calibration standards interspersed within the samples. When a continuing calibration or QC check standard fails to meet the QC criteria, all samples that were injected after the most recent standard that met the QC criteria must be reinjected.

10.8.11 Multi-level standards of each Aroclor are not required if the calculated concentration of any Aroclor in the sample extract falls within the 0.10µg/mL to 3.0µg/mL linear dynamic range established through initial calibration with the Aroclor 1016/1260 mix.

10.8.12 Sample injections may continue for as long as the continuing calibration standards, QC check standards and standards interspersed with the samples meet instrument QC requirements. At a minimum, standards are analyzed after every 20 samples and/or at the end of an analytical batch. The sequence ends when the entire batch of samples has been injected or when qualitative or quantitative QC criteria are no longer satisfied.

10.8.13 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If the retention time of any of the standards falls outside of the ±0.15 minute window, the system is out of control. Refer to section 10.10 for potential corrective actions.

10.8.14 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement of the capillary column or detector is warranted. The analyst may choose to rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Section 10.3 for the procedures to be followed for sample extract cleanup.

10.9 Qualitative identification

10.9.1 The identification of PCB Aroclors using an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes.

10.9.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification must be confirmed: (1) using a second GC column of dissimilar stationary phase (as in the dual-column analysis), (2) based on a clearly identifiable Aroclor pattern or (3) using another technique such as GC/MS .

10.9.3 When simultaneous analyses are performed from a single injection (the dual-column GC configuration), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed. When reporting results, the higher value of the two columns will be reported as long as they agree within 40% of each other. If not, the chromatograms should be carefully assessed for possible integration errors, calibration errors, or overlapping peak areas. If no errors are found, the higher result should still be reported along with advising the data user of the disparity between results on the two columns.

10.10 Chromatographic System Maintenance as Corrective Action

10.10.1 When system performance does not meet the established QC requirements, corrective action is required and may include one or more of the following actions.

10.10.2 Liner and Septa replacement: When retention time shift of 0.15 minutes or more is observed, or chromatography has otherwise deteriorated, replace septa, install clean liner, and remove

approximately 6 inches of guard column. Bake out the system for a few hours at 275°C. It may take 2 to 3 hours for the carrier gas flow to regulate itself. The system is now ready to be recalibrated.

10.10.3 Saturation Current Adjustment: When the baseline of either ECD detector becomes noisy, either the analytical GC columns need to be baked out at 275°C or the saturation current on the ECDs requires readjustment. The saturation current should be set at 35. This current setting is usually very stable, but needs to be readjusted every few years. Consult the Tracor 9001 operating manual for details.

10.10.4 Check of Splitter Connections: For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

10.10.5 Inspection of Metal Injector Body: Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material. Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the interior of the injector port with acetone and then rinse it with toluene, collecting the rinsate in the beaker. Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

10.10.6 Column Rinsing: The column should be rinsed with several column volumes of an appropriate solvent. Generally, a series of both polar and nonpolar solvents is recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases maybe the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

11. QA/QC:

11.1 KAR Laboratories has established a formal quality assurance program and maintains records to document the quality of all PCB data generated.

11.2 Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows (Section 10.7), continuing calibration verification (Section 10.8.3) and chromatographic analysis of samples (Section 10.10).

11.3 Initial Demonstration of Proficiency: KAR has demonstrated initial proficiency (with each sample preparation and determinative method combination) by generating data of acceptable accuracy and precision for target analytes in a clean matrix. Examples of such data are presented in Sections 12.1 through 12.3. The laboratory must also repeat the following operations whenever new analysts are trained or significant changes in instrumentation are made.

11.4 In the absence of recommended acceptance criteria for the initial demonstration of proficiency, as is the case for method 8082, KAR has adopted the range of 70 to130 percent recovery as guidance in evaluating the results. Given that the initial demonstration is performed in a clean matrix, the average recoveries of analyte from the four to seven replicates should generally fall with this range.

11.5 KAR is generally successful in satisfying the recovery criterion even at analyte concentrations near the reporting limit for the method. Therefore, whenever possible, the initial demonstration of proficiency is performed concurrently with the method detection limit study for a particular analyte.

12. Method Performance:

12.1 PCB Aroclor 1242 Sample Matrix: Aqueous

Replicate	True Value (µg/L)	Measured Value (µg/L)	Grubb's "T" Test (outlier if > 1.938)
1	.0500	.0396	.4499329
2	.0500	.0365	.0562416
3	.0500	.0457	1.224615
4	.0500	.0278	1.048634
5	.0500	.0261	1.264529
6	.0500	.0317	.5533449
7	.0500	.0450	1.135717

Mean:	.0361	% Recovery :	72.11
Std. Dev.:	.0079	Rel. % Diff:	21.84
Signal/Noise:	4.58	MDL:	.024749

12.2 PBC Aroclor 1242 Sample Matrix: Soil

Replicate	True Value (µg/kg)	Measured Value (µg/kg)	Grubb's "T" Test (outlier if > 1.938)
1	200.0	172.8	0.03
2	200.0	181.8	0.56
3	200.0	160.1	0.87
4	200.0	158.6	0.97
5	200.0	191.8	1.23
6	200.0	190.7	1.15
7	200.0	157.2	1.07

Mean:	173.2857	% Recovery:	86.64
Std. Dev.:	15.0944	Rel. %Diff:	8.71
Signal/Noise:	11.48	MDL:	47.441753

12.3 PCB Aroclor 1260 Sample Matrix: Soil

Replicate	True Value (µg/kg)	Measured Value (µg/kg)	Grubb's "T" Test (outlier if > 1.938)
1	200.0	183.8	0.98
2	200.0	169.5	0.96
3	200.0	189.6	1.77
4	200.0	172.9	0.50
5	200.0	174.1	0.34
6	200.0	170.8	0.78
7	200.0	175.3	0.17

Mean:	176.5714	% Recovery:	88.29
Std. Dev.	7.3769	Rel. % Diff.:	4.18
Signal/Noise:	23.94	MDL:	23.185681

12.4 Sample Quality Control for Preparation and Analysis: KAR Laboratories has established procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). These procedures include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

12.5 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. Generally, KAR uses a matrix spike and matrix spike duplicate pair, spiked with Aroclor 1242. However, when specific Aroclors are known to be present or expected in samples, an attempt will be made to use the appropriate Aroclor for spiking. In such cases, the laboratory may choose to use a single matrix spike in combination with a duplicate analysis of an unspiked sample.

12.6 The following table lists matrix spike control limits for aqueous and soil matrices:

PCB Mixture	Matrix	Spike Amount	Spike Recovery Control Limit Range, %
Aroclor 1242	Aqueous	0.2µg/L	10-118
Aroclor 1242	Soil	500µg/kg	33-126

12.7 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

12.8 See the appropriate KAR SOP for details regarding quality control procedures associated with sample preparation and analysis.

12.9 Surrogate recoveries. The analyst must evaluate surrogate recovery data from individual samples against the following KAR-generated surrogate control limits:

Surrogate Compound	Matrix	Spike Amount	Surrogate Recovery Control Limit Range, %
TCMX	Aqueous	0.2µg/L	6-68
DCB	Aqueous	0.2µg/L	29-102
TCMX	Soil	200µg/kg	0-134
DCB	Soil	200µg/kg	65-138

TABLE 1

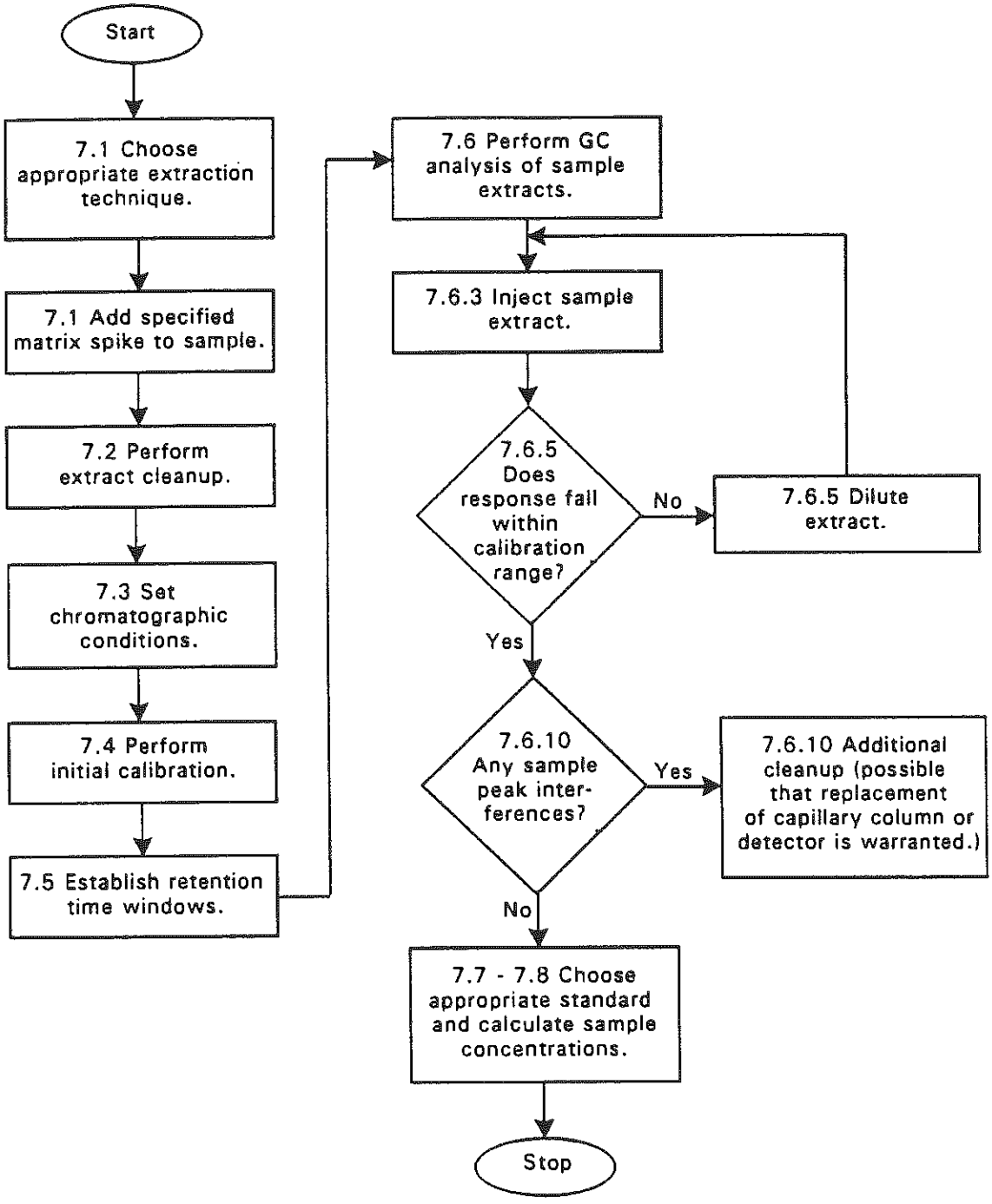
SPECIFIC PCB CONGENERS IN AROCLORS

		Aroclor						
Congener	IUPAC number	1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
23-DCB	5	X	X	X	X	X		
34-DCB	12	X		X	X	X		
244'-TCB	28*	X		X	X	X	X	
22'35'-TCB	44			X	X	X	X	X
23'44'-TCB	66*					X	X	X
233'4'6-PCB	110						X	
23'44'5-PCB	118*						X	X
22'44'55'-HCB	153							X
22'344'5'-HCB	138							X
22'344'55'-HpCB	180							X
22'33'44'5-HpCB	170							X

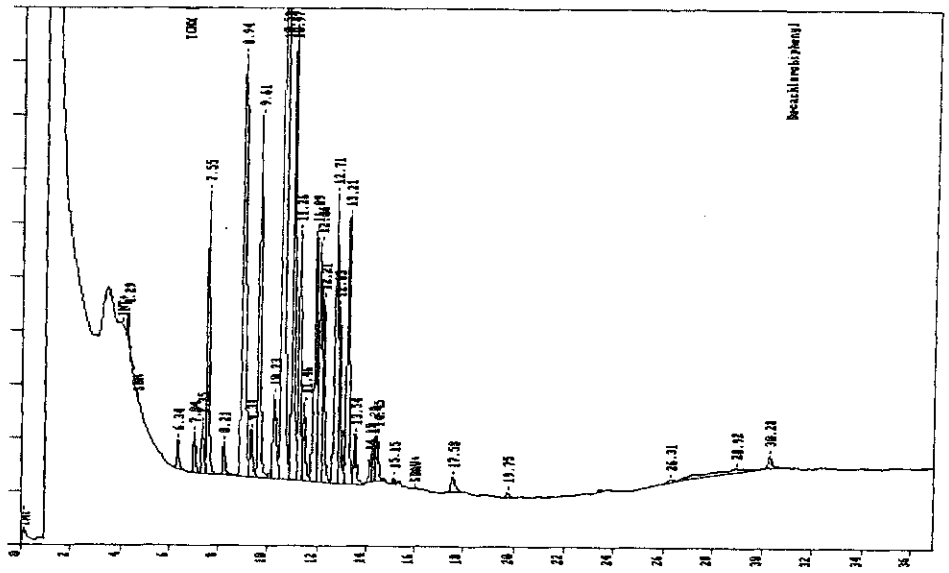
*Apparent co-elution of:
28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

FLOW CHART

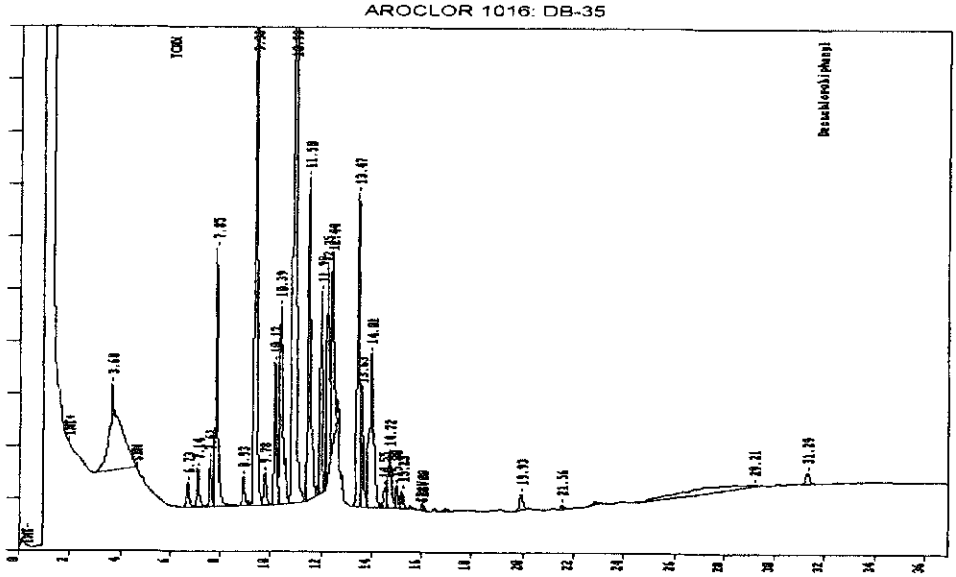
POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY



AROCLOR 1016: DB-5



AROCLOR 1016: DB-35



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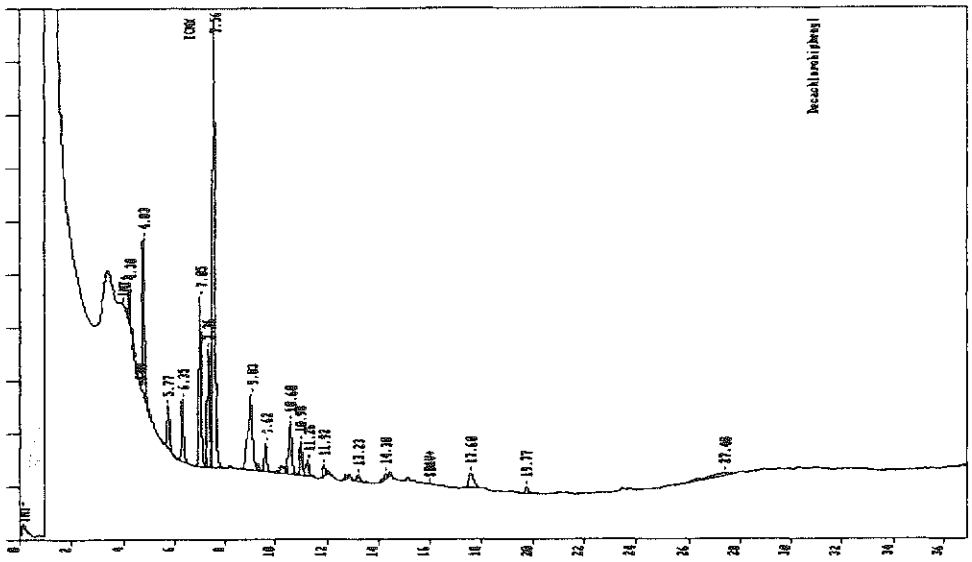

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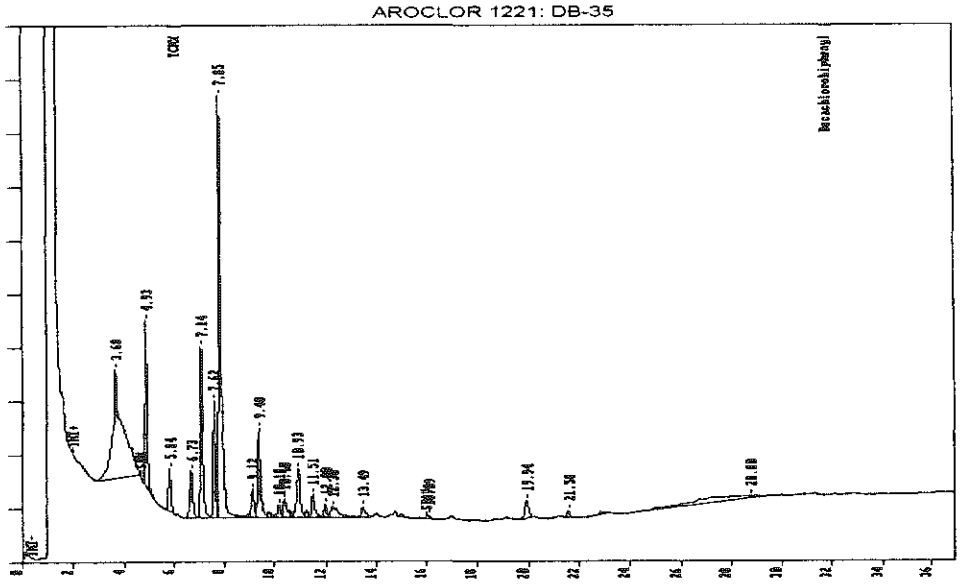

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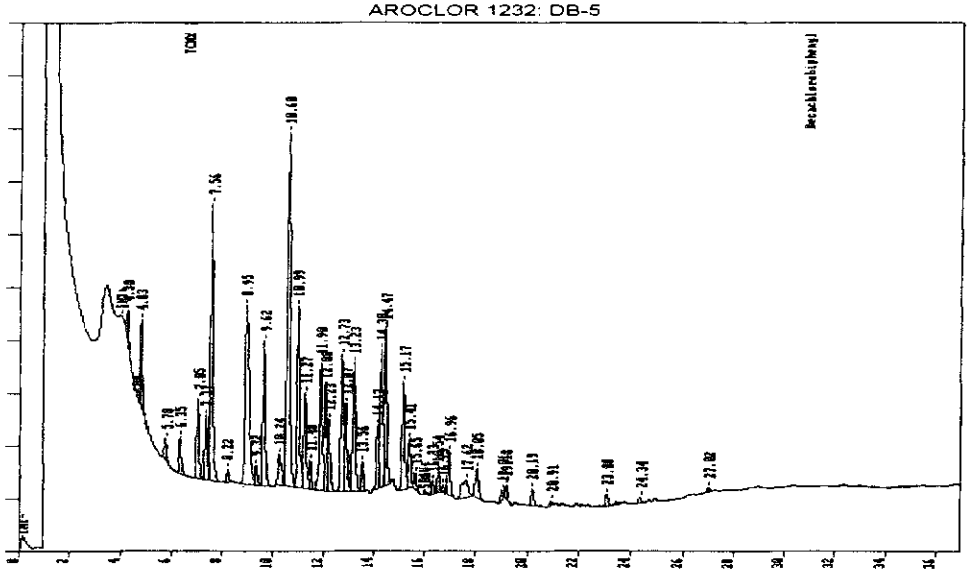
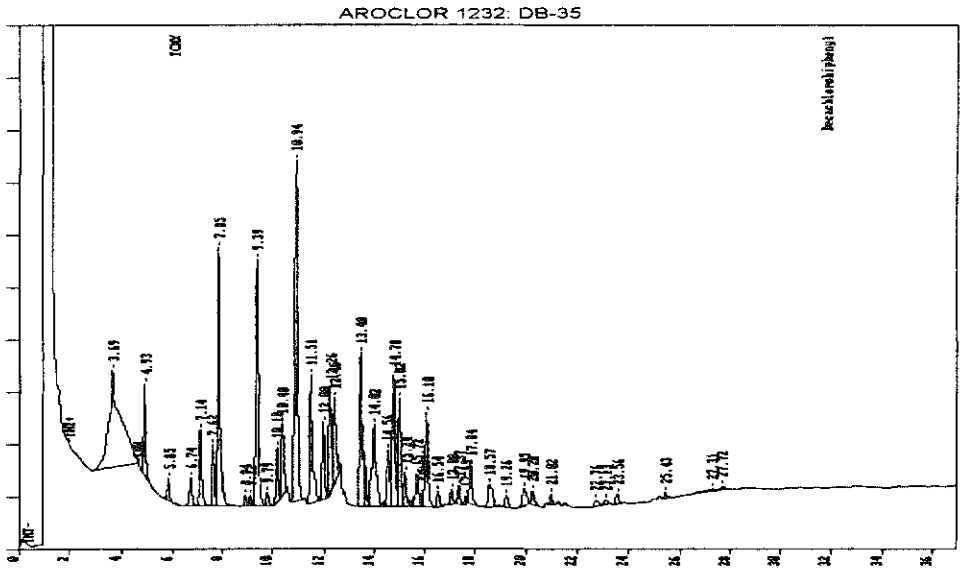


AROCLOR 1232: DB-35



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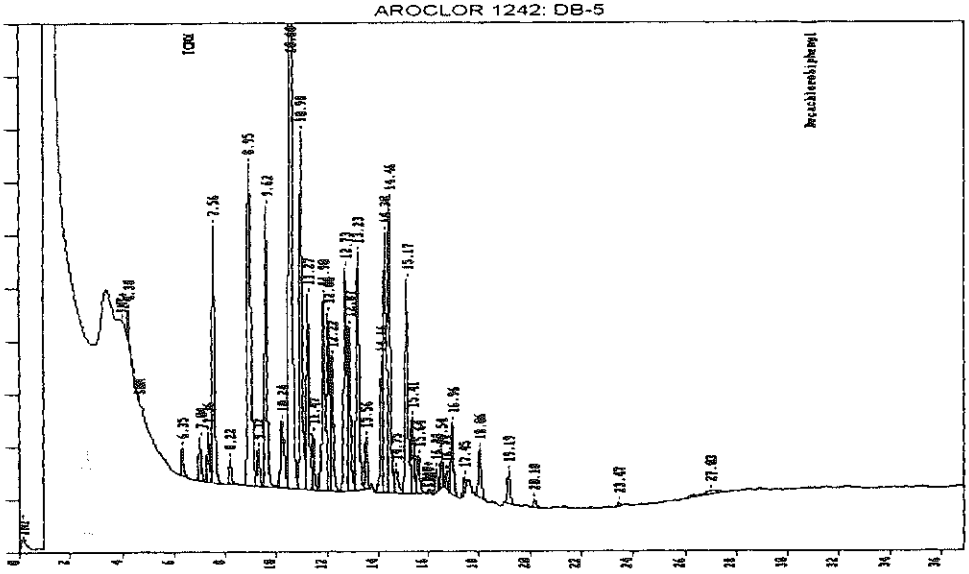

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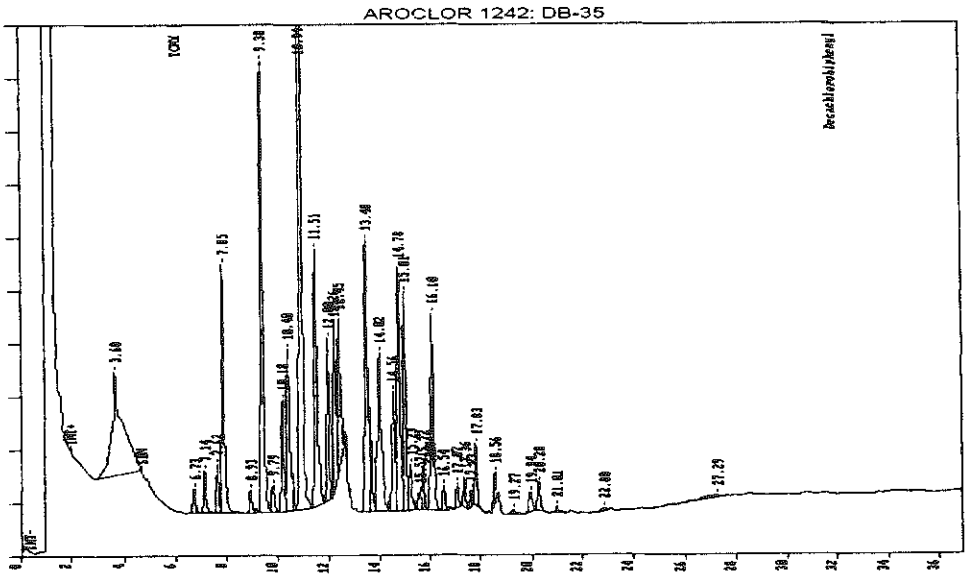
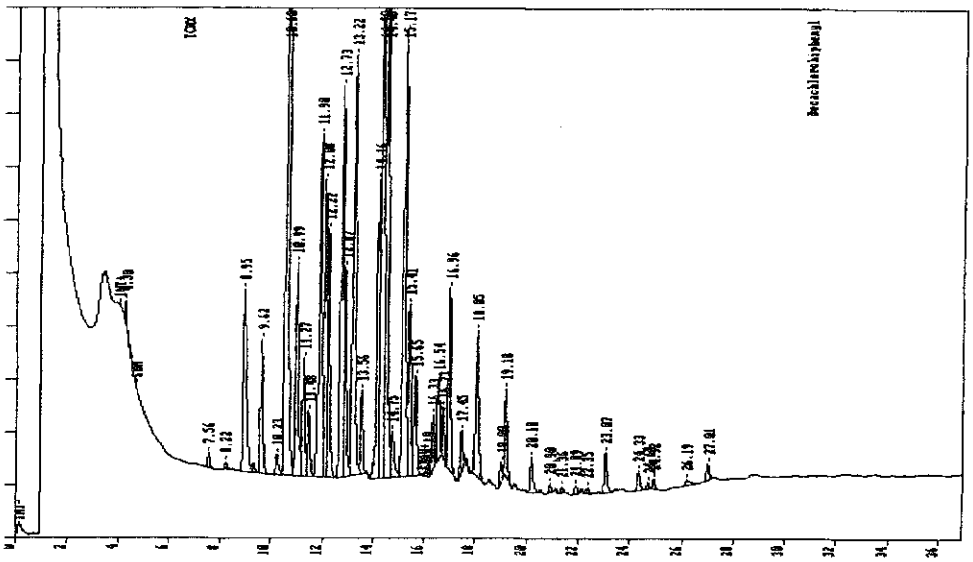


AROCLOR 1248: DB-5



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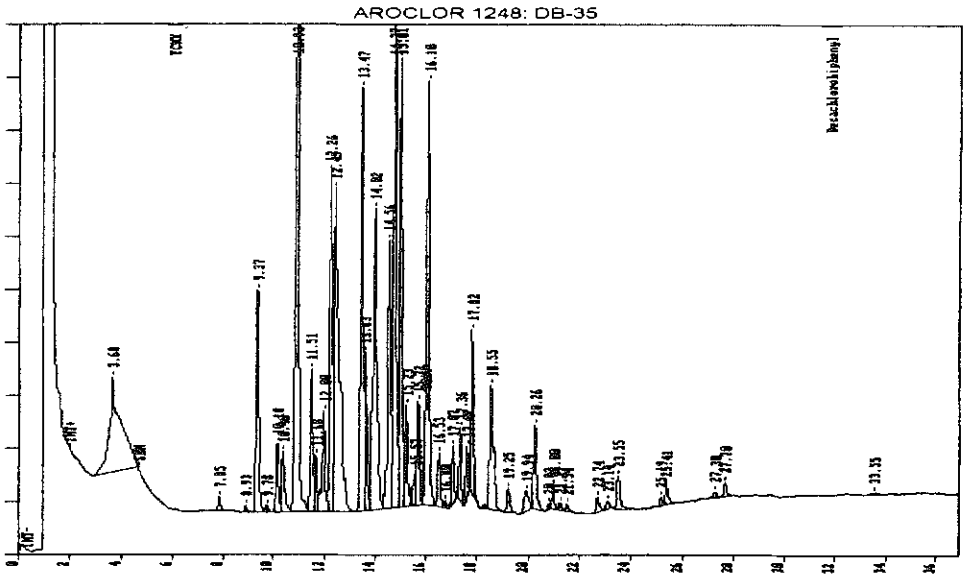
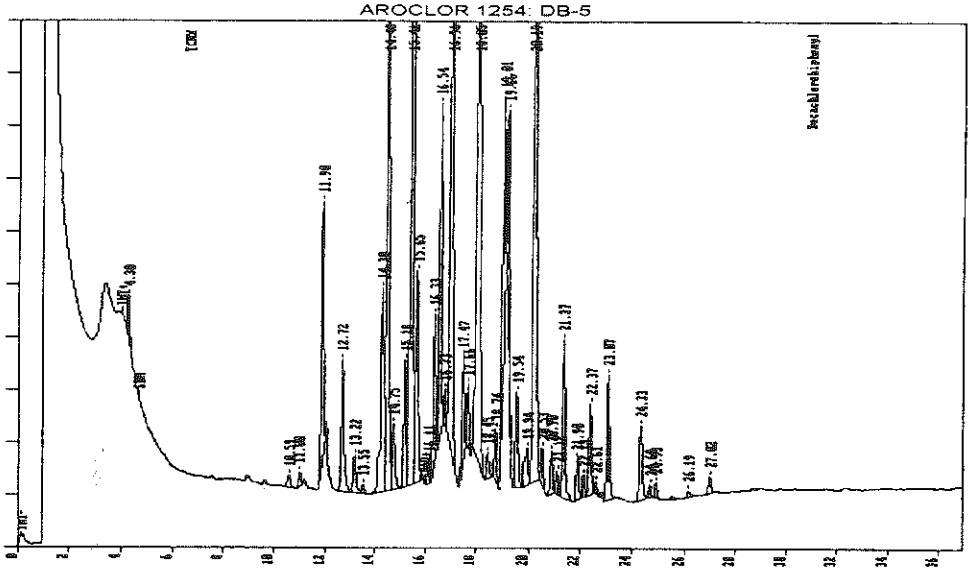


AROCLOR 1254: DB-5



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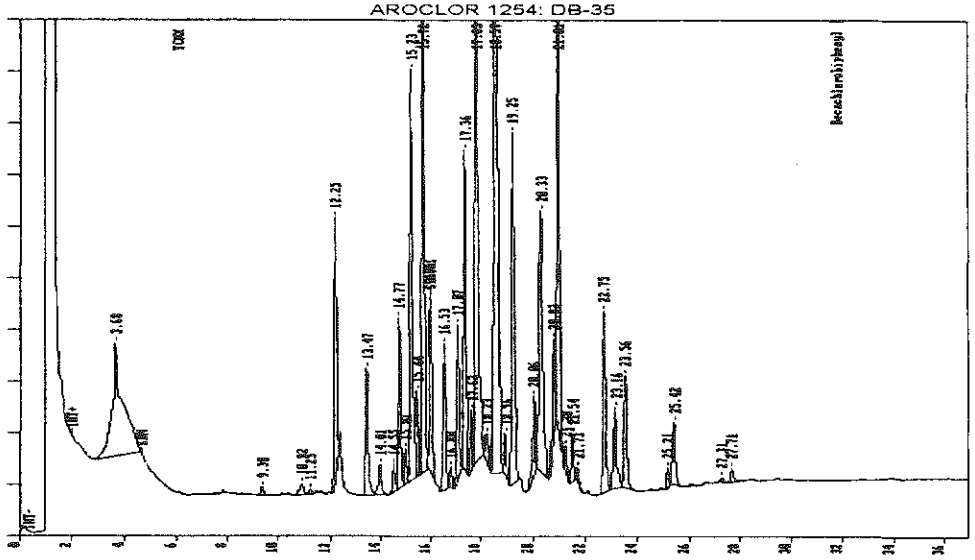

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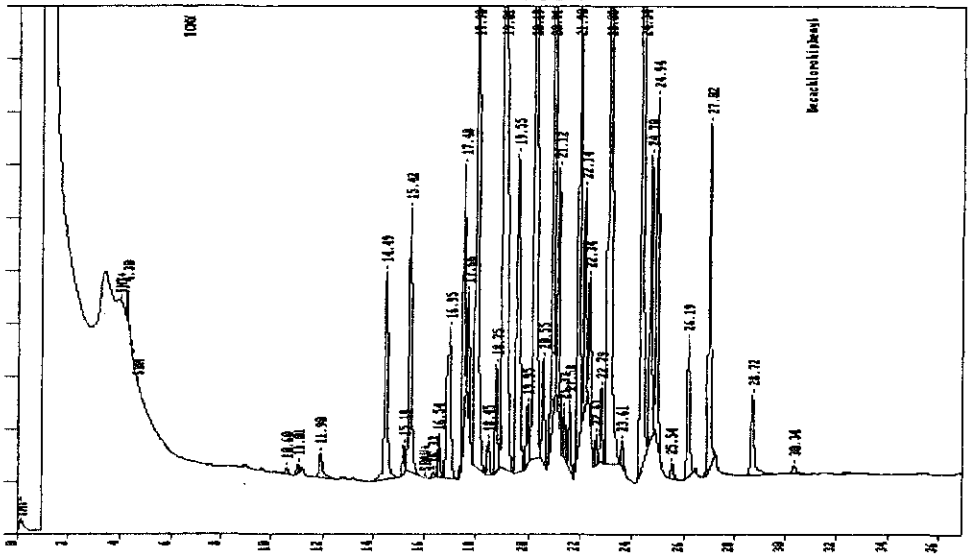

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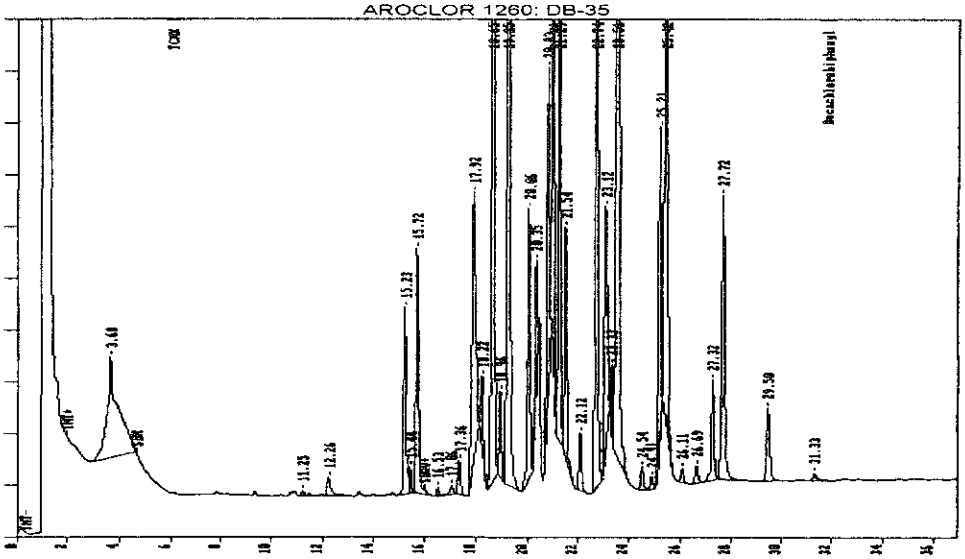

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To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-13-00
Kent Lawrence

Supervisor: _____ Date: 10/17/00
Michael Jaeger

Laboratory Director: _____ Date: 10/17/00
Michael Jaeger

QA Approval: _____ Date: 17-Oct-2000
Pollyann Nee

KAR LABORATORIES, INC.

SAMPLE PREPARATION METHODS

AUTHORIZED COPY

SOP No.: KM301.01
Date issued: 10/17/00
Next revision due: 10/01

STANDARD OPERATING PROCEDURE

Aqueous Sample Preparation by Acid Digestion for Trace Metals Analysis using the Environmental Express Block Digester

References : "Standard Methods for the Examination of Water and Waste," 1992, 19th Edition

EPA's "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, 3rd Edition

Application: This is an acid digestion procedure for the preliminary treatment of aqueous samples and TCLP, SPLP, and ASTM extracts for trace metals analysis.

Summary : A representative sample is digested with acid and evaporated to a low volume on a block digestion system. The sample is allowed to cool, adjusted to an appropriate volume and filtered, if needed.

Apparatus :
HotBlock™ (block digestor from Environmental Express)
Polypropylene concave ribbed watch glasses
50mL polypropylene digestion vessels with caps
Sample vessel foam tray
Plastic rack for sample vessels
FilterMate™ 2µ (filter device)
Digestion logbook
Optifix® dispenser
Eppendorf® pipettors fixed volumes: 1000µL, 100µL

Safety : All chemicals and samples should be handled with care. Lab coats and gloves and safety glasses must be worn. The mixing of acid with samples must be done in a fume hood. Samples may react violently with acid, so when adding acid to the samples, face the top of the vessel towards the back of the fume hood and always add the acid **slowly**. Some samples will emit fumes and care should be used when measuring or moving samples.

Chemicals & Reagents :

Concentrated nitric acid, metals grade
Concentrated hydrochloric acid, metals grade
Custom spike solution - purchased from VHG LABS
Reagent water, deionized

Procedure :

1) Label the sample vessel with the sample number using a permanent marker. Mix the sample well and measure 50 mL using the calibration line on the side of the sample vessel. A smaller sample volume may be used if high analyte concentrations are expected. Record the initial sample volume in the sample logbook.

2) Using a deionized water squeeze bottle, add 50mL of reagent water for the lab method blank (LMB) and 50mL of reagent water for the lab control sample (LCS).

3) Using a 100µL Eppendorf® pipettor add 100µL of custom VHG spike solution to the LCS and to all other QC spike samples.

4) Using the Optfix® dispenser add 2mL of conc. nitric acid slowly to each vessel. Cover with a ribbed watch glass and place on the sample rack. Place the sample rack in the HotBlock™.

   NOTE: If the sample requires analysis for either antimony, silver or tin, use 2mL of conc. nitric acid and 2mL of hydrochloric acid. This will improve the spike recoveries of these elements.

5) Turn on the Hotblock™ in the fume hood (the temperature is preset at 93°C). Heat the samples slowly without boiling until the volume has been reduced to 10-20mL. Care should be taken so the samples do not bump. Record the temperature of the Hotblock™ in the log book. Then remove all samples from the HotBlock™ and cool to approximately room temperature.

6) Adjust the final volume of digestate to 50mL with deionized water using a squeeze bottle. Filter if needed using the FilterMates™. Cap the digestion vessel and place it in the foam sample rack. Record the final volume of digestate in the sample logbook.

Quality control: 1) For each daily prepared batch, a laboratory method blank (LMB) must be carried through the entire sample preparation and analytical process to demonstrate the absence of contamination. If a contamination problem is observed, it must be isolated and corrected.

2) For each daily prepared batch, a laboratory control sample (LCS) must be carried through the entire sample preparation and analytical process to demonstrate adequate analyte recovery.

3) A minimum of one duplicate and one spike must be processed for every ten samples.

4) Any dilution performed must be recorded in the sample logbook and on the sample vessel.

5) Any digestate that is inadvertently allowed to go to dryness in the HotBlock™ must be discarded. The sample preparation process must then be repeated using a new digestion vessel and additional sample.

6) The HotBlock™ has a preset temperature of 93 °C (90-95 °C is the method requirement) and should not be changed without supervisor approval. The HotBlock™ temperature must be monitored and recorded in the logbook. Under standard conditions, a batch of samples may be processed in approximately four hours.

7) The lot number of acids and spike solution used in the preparation of samples must be recorded in the logbook.

8) The lot number of the sample vessels used must be recorded in the logbook.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-16-00
David Lilac

Supervisor: _____ Date: 10/17/00
Michael Jaegar

Laboratory Director: _____ Date: 10/17/00
Michael Jaeger

QA Approval: _____ Date: 17-Oct-2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE

Acid Digestion of Sediments, Sludges and Soils

Principal Reference:

EPA's *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd Edition, Update III, December, 1996.

Standard Methods for the Examination of Water and Waste, 1992, 18th edition, section 3050.

Application:

This method describes two separate digestion procedures for sediments, sludges, and soil samples; one for analysis by flame atomic absorption (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES), and one for analysis by graphite furnace atomic absorption (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES/FLAA or GFAA/ICP-MS for all the listed metals as long as acceptable detection limits are achieved. Alternative determinative techniques may be used if they are scientifically valid and acceptable QC performance is achieved. Other elements and matrices may be analyzed by this method if acceptable QC performance is achieved. The recommended determinative techniques for each element are listed below:

FLAA or ICP-AES		**GFAA or ICP-MS**
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Antimony
Barium	Molybdenum	Beryllium
Beryllium	Nickel	Cadmium
Cadmium	Potassium	Chromium
Calcium	Silver	Colbalt
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		

This method is **not** a total digestion technique for most samples. It is a strong acid digestion that will dissolve most elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not very mobile in the environment. If absolute total digestion is required, use Method KM3052.

Summary of Method:

A representative subsample of approximately 2.5g (wet weight) is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume by heating and then diluted to a final volume of 100mL. For ICP-AES or FLAA analysis, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. The digestate is then diluted to a final volume of 100mL.

Apparatus:

150mL Griffin beakers, Pyrex®
Watch glasses, ribbed, concave
Whatman #42 filter paper, 12.5 cm
Volumetric flasks, Class A, 100mL
Funnels, plastic
Sample bottles, 125mL, Nalgene®
Polyethylene squeeze (wash) bottle, 500mL, Nalgene®
Hot plate, Thermodyne®
Thermometer, capable of measuring to at least 125°C
Acid dispenser, OPTIFIX®
Fixed volume pipetters, 100 and 1000µL, calibrated, Eppendorf®

Chemicals & Reagents:

Nitric acid (HNO_3), concentrated, "Trace Metal" Grade, 2.5L in glass, (Fisher Cat. #A509- 212)
Hydrochloric acid (HCl), concentrated "Trace Metal" Grade, 2.5L in glass, (Fisher Cat. #A508-212)
Reagent water equivalent to ASTM Type 1 (ASTM D 1193) >18 Megohm/cm resistivity
Hydrogen peroxide (H_2O_2), 30%, 4L, (Fisher Cat. #H325-4)
Spike Solution - Custom made (Spex Cat. #XKAR-1)

Sample Handling:

All sample containers must be demonstrated to be free of metal contamination at or below the reporting limit. Plastic and glass containers are both suitable. Non-aqueous samples should be stored at 4°C and analyzed within six months.

Interferences:

It may be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

Safety:

The mixing of acid with samples must be done in a fume hood. Samples may react violently with acid or produce toxic fumes. Add acid to samples **slowly**, tilting the opening of the beaker towards the back of the fume hood. Some samples may emit organic vapors. Care should be used when weighing or moving samples.

The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices should be practiced at all times. Safety glasses and acid-resistant gloves should be worn at all times when handling samples or reagents, or when in the vicinity of others handling these items.

Procedure:

Refer to Attachment I for flow chart.

1. Mix the sample well and weigh out approximately 2.5g of a representative portion of wet sample into a 150mL beaker. Label the beaker with the sample ID and mass, and record the information in the Metals Prep Logbook.

   NOTE: The final results for a municipal sludge sample is based on its dry weight. Special consideration must be given to the amount of sample to digest. Use the following formula for calculating the mass of sample to digest (this formula also aids in calculating a detection limit based on dry weight):

$$\text{grams to digest} = \frac{100}{\%\ \text{total solids}}$$

   Example: A sludge sample consists of 10.0% total solids. The correct mass to digest would be 10g. All digested sludges are diluted to 100mL.

2. Add 10mL of reagent water to each sample. To separate beakers, add 10mL of reagent water for the lab method blank (LMB) and for the lab control sample (LCS).
3. Add 1.0mL of spike solution to the LCS and all other samples designated for matrix spikes using an fixed volume 1000µL calibrated pipetter.
4. For the digestion of samples for analysis by GFAA or ICP-MS, add 10mL HNO_3, mix the slurry and cover with a ribbed watch glass. Heat the sample to 93 ± 2°C and reflux for 10-15 minutes without boiling.
5 Allow the sample to cool, add 5mL of concentrated HNO_3, replace the cover and reflux for 30 minutes. If brown fumes are generated (indicating oxidation of the sample by the HNO_3), repeat this step until no brown fumes are given off by the sample (indicating the complete reaction with HNO_3).

NOTE: All steps requiring the use of acids should be conducted in a fume hood by properly trained personnel using appropriate laboratory safety equipment.

6. Heat samples at 93 ± 2°C (taking care not to allow the samples to bump) until the volume has been reduced to 5-7mL. Reject any sample that goes to dryness and redigest. If an oil layer forms on top of the liquid, use a stir bar on the heated stir plate to help prevent bumping.
7. Remove from the hot plate and let cool. Add 2mL of reagent water and 3mL of 30% H_2O_2. Cover the vessel with a watch glass and return the covered vessel to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to vigorous effervescence. Heat until effervescence subsides and cool the vessel.
8. Continue to add 30% H_2O_2 in 1mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10mL 30% H_2O_2.

Continue heating the acid-peroxide digestate at 93± 2°C without boiling until the volume has been reduced to approximately 5mL.

9. **For analysis by GFAA or ICP-MS:** After cooling, filter the digestate through Whatman No. 42 filter paper, washing frequently with reagent water from a squeeze bottle, and collect the filtrate in a 100mL volumetric flask. Bring up to volume with reagent water and store in a labeled 125mL plastic sample bottle for analysis. The diluted digestate solution contains approximately 5% (v/v) HNO_3.
10. **For the analysis of samples for FLAA or ICP-AES:** Add 10mL conc. HCl to the sample digestate from step 8 and cover with a watch glass. Place the sample on the hot plate and reflux at 93 ± 2°C for 15 minutes. Filter the digestate through Whatman No. 42 filter paper , washing frequently with reagent water from a squeeze bottle, and collect filtrate in a 100mL volumetric flask. Bring up to volume with reagent water and store in labeled 125mL plastic sample bottle for analysis.

Calculations:

The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided. The determination of percent solids must be performed on a separate homogeneous aliquot of the sample as specified in KAR SOP KG462.

Quality Control:

For each batch of samples processed, a Laboratory Method Blank (LMB) must be carried throughout the entire sample preparation and analytical process. This blank is essential in determining if samples are being contaminated. Analyze one LMB for every batch of 20 samples or less.

A Laboratory Control Sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS is essential in determining if analytes are being lost in the sample preparation process. Analyze one LCS for every batch of 20 samples or less.

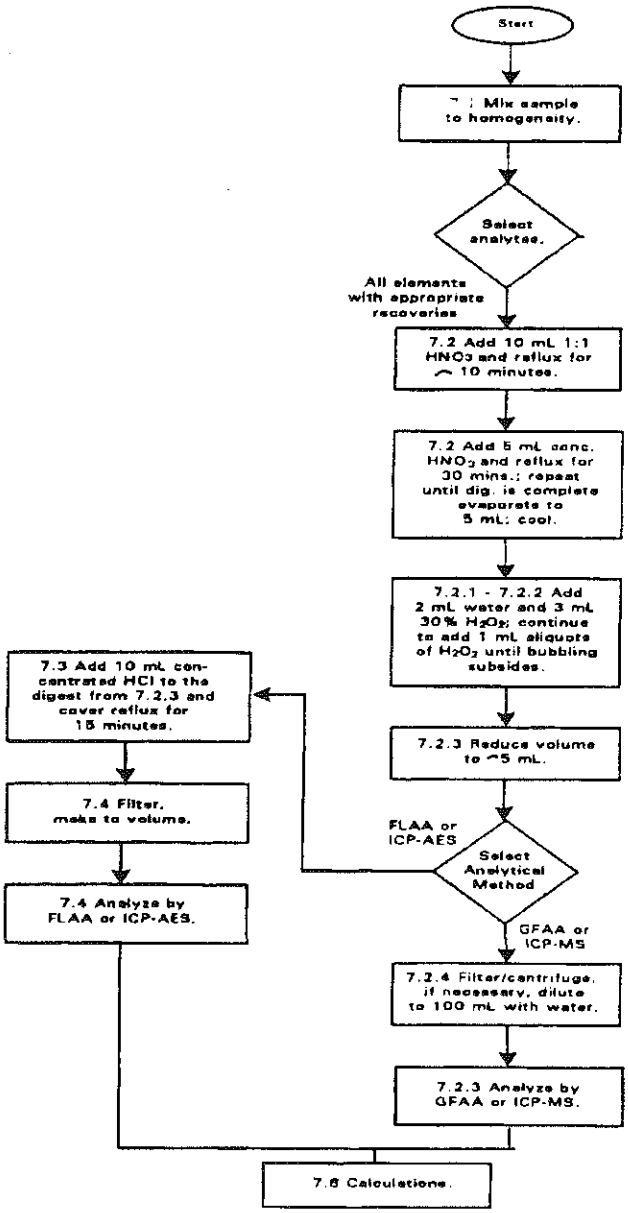
Analyze one digested matrix spike and one digested matrix spike duplicate for every 10 samples. Use a fixed volume pipetter for spiking.

Record in logbook, hot plate temperature, lot # of acids used, lot # of custom spiking solution, and volume of spike used.

No down arrows are allowed for sample weights, record the exact weight.

Note: There is one attachment to this SOP.

FLOW CHART FOR METHOD 3050B
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS
ATTACHMENT I



Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-11-00
David Lilac

Supervisor: _____ Date: 10/12/00
Michael Jaeger

Laboratory Director: _____ Date: 10/12/00
Michael Jaeger

QA Approval: _____ Date: 12-Oct-2000
Pollyann Nee

Method: KM7470
Revised Date: 2/18/93

STANDARD OPERATING PROCEDURE

Aqueous Sample Preparation for Mercury Analysis

Principle

References : EPA's "Test Methods for Evaluating Solid Waste", SW-846, Vol. 1A, Method 7470.

Application : This SOP is a cold-vapor atomic absorption procedure for determining the concentration of mercury in extracts, aqueous wastes, and groundwaters. All samples must be subjected to an appropriate dissolution step prior to analysis.

Summary of Method : Prior to analysis, the liquid samples must be prepared according to the procedure outlined in this method. The actual analysis of the samples is done with the cold-vapor atomic absorption method using a continuous flow hydride vapor generator. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The mercury vapor absorbs radiation at 253.7 nm and the absorbance is measured as a function of mercury concentration.

Interferences : Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide and sodium sulfide do not interfere with the recovery of added inorganic mercury.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because during the oxidation step, chlorides are converted to free chlorine, which also absorbs at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride.

Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type interference is present.

Apparatus & Materials :

- Aluminum foil
- Watch glasses
- 200 mL beakers
- 25 mL pipetter
- 10 mL pipetter
- Water bath
- Plastic graduated cylinders

Reagents :

- Potassium permanganate
- Potassium persulfate
- Stannous chloride
- Sodium chloride
- Hydroxylamine hydrochloride
- Conc. Nitric Acid (Metals Grade)
- Conc. Sulfuric Acid (Metals Grade)
- Mercury Stock Standard, 1000 ppm
- Mercury Working Standard, 1 ppm = 1 ug/mL
  Add 0.100 mL of the 1000 ppm stock standard to a 100 mL volumetric and bring up to volume with 0.4% HNO_3. This should be made fresh each time samples are run.
- Potassium Permanganate Solution, 5% (w/v)
  Dissolve 25 g of potassium permanganate in 500 mL deionized water.
- Potassium Persulfate Solution, 5% (w/v)
  Dissolve 25 g of potassium persulfate in 500 mL deionized water.
- Stannous Chloride Solution, 20% (w/v)
  Dissolve 50 g stannous chloride in 65 ml HCl. Gentle heating may be necessary to get all of the stannous chloride into solution. Bring up to volume of 250 ml with deionized water.
- Sodium Chloride-Hydroxylamine Hydrochloride Solution
  Dissolve 60 g of sodium chloride and 60 g of hydroxylamine hydrochloride in deionized water and dilute to 500 mL. (Hydroxylamine sulfate may be used instead of hydroxylamine hydrochloride).

Safety : All chemicals and samples should be handled with care.

Lab coat, gloves and safety glasses should be worn.

Procedure :

1. Set-up water bath and have it heating up while the standards and samples are being prepared.
2. Transfer 0, 0.05, 0.1, 0.2, 0.5, and 1.0 ml aliquots of the working standard (1ppm) into beakers with 100 ml D.I. water. Label the beakers, Bl, 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 5.0 mg/L, and 10.0 mg/L, respectively.
3. For each aqueous sample transfer 100 ml of sample into a labeled beaker.
4. Add 5 mL concentrated sulfuric acid with the 10 mL pipetter to each of the standards and samples.
5. Add 2.5 mL of concentrated nitric acid, using the 10 mL pipetter, to each of the standards and samples. Then swirl beaker.

6. Add 15 mL of 5% potassium permanganate to each of the standards and samples. Use the 25 mL pipetter. Swirl beaker and allow samples to stand for 15 minutes. Some samples may require additional permanganate. If the purple color does not persist for at least 15 minutes, add additional portions of potassium permanganate solution.
7. Using the dispenser, add 8 mL potassium persulfate to each of the standards and samples.
8. Cover each beaker with a watch glass and seal with aluminum foil.
9. Put the beakers into the water bath. Heat in the water bath for 2 hours at 95° C.
10. Cool samples to room temperature and add 6 mL of sodium hydroxylamine hydrochloride to each of the standards and samples, (using the dispenser), just prior to analysis. This reduces the excess potassium permanganate. Mix each beaker until all of the excess potassium permanganate has been reduced.
11. Analyze the standards and samples using the hydride generator. Refer to the SOP for the hydride generator for complete set-up and usage instructions.

Calculations : For calculating standard concentration, $C_1V_1 = C_2V_2$.

QA/QC : A laboratory method blank must be run with each batch of samples. If contamination is detected, the source must be isolated, corrected and documented.

A spike and a duplicate must be done for each set of 10 samples. If the duplicate or spike is not within specified recovery limits, the problem must be isolated and corrected.

The lowest reporting level: 0.0002 mg/L

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STANDARD OPERATING PROCEDURE

Closed-System Purge & Trap and Extraction for High-Level Volatile Organics

PRINCIPAL REFERENCE: U.S. EPA Method 5035, SW-846, 3rd Edition, Update III, December, 1996.
MDEQ Method DEQ ORGLAB-11, March 26, 1998.

SUMMARY: This method describes the sampling procedure of solid materials (soils) for high-level volatile organic compounds in the concentration range >50 *ug*/kg. The sample is collected using a sampling device which minimizes the disturbance of the sample in order to reduce the loss of analytes. The sample is then preserved and extracted in methanol. At the time of analysis, an aliquot of the methanol is removed and added to organic free water. Internal standards and surrogates are added to the sample and it is then loaded into a purge vial. The sample is then introduced to the instrument which will add surrogates and internal standards. The vial containing the extract is then purged with an inert gas. The volatile organic compounds are stripped from the extract and swept by the inert gas through the transfer line to an adsorbent trap. When vial purging is complete the trap is heated and backflushed with helium to desorb the trapped sample components into a Gas Chromatograph for analysis by an appropriate determinative method. A separate bulk container is collected to determine solids content. Results are reported based on dry sample weight.

INTERFERENCES:

1. Major contamination sources include volatile materials in the laboratory, field and impurities in the inert purge gas or methanol. Care must be taken to avoid potential sources of contamination in the field. Preparation blanks are analyzed in the same manner as the samples to monitor laboratory or field impurities. When potentially interfering peaks are noted in system blanks and the purge gas is determined to be the source, the analyst should take appropriate corrective action to identify and correct the contaminant source.

2. Sample can be contaminated by the diffusion of volatile compounds (particularly methylene chloride and fluorocarbons) through the sample container septum during shipment and storage. Use a trip blank, consisting of a sample container carried through sampling and storage, as a check for such contamination.

3. Contamination by carryover can occur when low concentration samples follow unusually high concentration samples. When possible, a reagent blank should follow the analysis of the high concentration sample. However, if another sample follows, it should be shown to be clean of the high concentration target analytes, or re-analyzed after demonstrating carryover from high concentration target analytes has been eliminated.

APPARATUS:

1. Syringes
   5mL, Luerlock, Hamilton 1005.
   10*u*L, Hamilton 1701
   25*u*L, Hamilton 1702
   100*u*L, Hamilton 1710
   250*u*L, Hamilton 1725
   500*u*L, Hamilton 1750
   1000*u*L, Hamilton 1001
2. Volumetric flasks-Class A: 10, 50, 100, 500, 1000mL with ground glass stoppers
3. Analytical balance, Fisher Scientific Model No. XT 410, 0.01g sensitivity.
4. Pre-tared 40ml vials with 10ml purge & trap grade methanol and Teflon® -lined screw caps, QEC Part No. 2112-40CH_3T.
6. En Core™ sampler, 25g, En Novative Part No. EN250002
7. En Core™ sampler, 5g, En Novative Part No. EN050002
8. Disposable glass pipets, 25mL, VWR Part No. 53047-616
9. Sample vials, 40mL, QEC Part No. 2112-40mL
10. Terra Core™ soil sampler, 5g, En Novative.

REAGENTS:

1. Purge & Trap grade Methanol, Burdick & Jackson, Catalog No. 232-235
2. Purge & Trap grade Methanol, 25 mL ampules, Nalge Nunc International
3. Reagent water, organic free

SAMPLE COLLECTION, PRESERVATION and HANDLING:

A. Sample Collection using En Core™ Sampler (Lab Preservation)

1. Hold coring body and push plunger rod down until small o-ring rests against tabs. This will assure that plunger moves freely.
2. Depress locking lever on EnCore™ T-handle. Place coring bottle, plunger end first, into open end of T-handle, aligning the slots on the coring body with the locking pins in the T-handle. Twist coring body clockwise to lock pins in slots. Check to ensure sampler is locked in place. Sampler is ready for use.
3. Turn T-handle with T-up and coring body down. This positions plunger bottom flush with bottom of coring body (ensure that plunger bottom is in position). Using T-handle, push sampler into soil until coring body is completely full. When full, small o-ring will be centered in T-handle viewing hole. Remove sampler from soil. Wipe excess soil from coring body exterior.
4. Cap coring body while it still is on the T-handle. Push and twist cap over bottom until grooves on locking arms seat over ridge on coring body. Cap must be seated to seal sampler.
5. Remove the capped handler by depressing locking lever on T-handle while twisting and pulling sampler from T-handle.
6. Lock plunger by rotating extended plunger rod fully counter-clockwise until wings rest firmly against tabs.
7. Attach completed circular label (from EnCore™ sampler bag) to cap on coring body.
8. Return full EnCore™ sampler to zipper bag. Seal bag and put on ice for shipment to laboratory. THE SAMPLE MUST BE PRESERVED WITH METHANOL WITHIN 48 HOURS OF COLLECTION.
9. Collect an additional representative subsample of soil in a 2 oz. glass jar for total solids determination.

B. Sample Collection with Field Preservation

1. Select a Pre-tared 40ml vials with 10ml purge & trap grade methanol and Teflon® -lined screw caps. Record the tare weight on the vial label.
2. Select a Terra Core™ soil sampler. Lock the plunger in the position parallel to the T-handle.
3. Push and twist the end of the soil sampler into the soil sample until the soil begins to push the plunger up from the T-handle. Immediately put the open end of the sampler into the pre-tared

40ml vial. Twist the plunger so it is perpendicular to the T-handle. Depress the plunger slowly until all the sample is deposited in the glass bottle. Be careful to not drop the sample from too high above the methanol to avoid any splashing and subsequent loss of the methanol.

4. Repeat step 3.
5. Quickly cap the glass bottle and re-weigh, recording the weight to 0.01 gram. The difference between the weight in step 1 and step 4 is the sample weight. The sample weight should be approximately 10.0 gm.
6. Store the sample at 4°C.
7. Collect an additional representative subsample of soil in a 2 oz. glass jar for total solids determination.

Sample Collection Technique	Holding Times from Date and Time of Collection to:	
	Methanol addition	Analysis
EnCore™ sampler	48 hours	14 days
Disposable sampler	Immediately	14 days

PROCEDURE: A. Sample Preparation

1. Samples received in EnCore™ sampler
   a. Using a 2 oz. glass sample bottle for 25 g. EnCore™ samplers or a 40mL vial for 5 g. EnCore™ samplers, obtain the tare weight and record to 0.01 g.
   b. Attach EnCore™ sampler to EnCore™ Extrusion Tool by depressing locking lever on extrusion tool and placing sampler plunger end first into open end of extrusion tool, aligning slots of coring body with pins in extrusion tool.
   c. Use pliers to break locking arms on cap of EnCore™ sampler. Do not remove cap at this time.
   d. Turn coring body clockwise until it locks in place. Release locking lever.
   e. Rotate and gently push extrusion tool plunger knob clockwise until plunger slides over wings of coring body. When properly positioned, the plunger will not rotate.
   f. Remove the cap from sampler and push down on plunger knob of the EnCore™ extrusion tool to release the soil core into the tared container.

g. Cap the container and re-weigh. Record the weight to 0.01 gram. The difference between this weight and the weight in step A.1.(a) is the sample weight.
h. Add a volume of methanol to the sample vial to maintain a 1:1 weight/volume ratio with the sample. Store the sample at 4°C until analysis.

2. Samples Field-Preserved with Methanol
   a. Re-weigh the field-preserved vials to determine if a significant loss of methanol has occurred. Reject any samples with a loss greater than 0.5mL.

3. Total Solids Determination
   a. Refer to KAR SOP KG462 for Total Solids Determination

B. Analysis

1. Sonicate the sample for 20 minutes. Allow to settle completely prior to analysis.
2. Fill a 50mL volumetric flask with organic free water and using a 1000*u*L gas-tight syringe, add 1000*u*L of the methanol extract. Invert the flask several times to mix.

   NOTE: Smaller volumes of sample may be used if screening methods or prior analysis indicates target components will be above the linear range.

3. Transfer the diluted sample to a 40 mL VOA vial and load in the autosampler tray for analysis.

QUALITY CONTROL:

1. Method blanks should be prepared with each set of prepared samples and/or bottle or lot of methanol ampules. The blank must be prepared in the same environment using the same reagents and apparatus as the samples.
2. A trip blank must accompany each set of sample bottles through the sampling process and shipping. It will consist of the same bottle used in sampling along with a similar volume of the Purge & Trap grade methanol which will be used in sample preparation.
3. Refer to the appropriate SOP for internal standard solutions, surrogate solutions, QC requirements and operating conditions.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: David Z Bailey Date: 10-24-00
Dave Bailey

Supervisor: Julie Rumsey Date: 10-24-00
Julie Rumsey

Laboratory Director: Michael Jaeger Date: 10/24/00
Michael Jaeger

QA Approval: Pollyann Nee Date: 24-Oct-2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE

Separatory Funnel Extraction by EPA Method 3510C

Principal Reference : Separatory Funnel Liquid-Liquid Extraction, Method 3510C EPA SW-846.

Application : This procedure is used for the solvent extraction of compounds from aqueous samples to be analyzed for semi-volatile organic compounds by EPA Method 8270 or polychlorinated biphenyls (PCB) by EPA Method 8082.

Interferences : (1) Phthalate esters, found in many plastics, are a major source of contamination. Therefore, it is crucial that samples and reagents contact glass or Teflon **only**. In particular, the following precautions must be taken:

- Plastics may not be used in any part of the procedure (including plastic pipets and squirt bottles).
- Gloves or glove powder must not come in contact with any surface in which the sample or extract is exposed.

(2) PCB samples may be subjected to cleanup methods to remove interferences if necessary. (See SOPs KO8081 and KO8082.)

Safety : The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, $MeCl_2$ and PCBs are suspected human carcinogens. Solvents, samples, reagents and spiking and surrogate solutions should be treated as potential health hazards and exposure to them should be minimized. A reference file of Material Safety Data Sheets (MSDS) is available to all employees and the MSDS for each chemical used should be read prior to use. $MeCl_2$ must be used in a fume hood to avoid inhaling the vapor. The hood must be operated by a safe face velocity as monitored by the velocity alarm on the hood. Gloves and safety glasses must be worn to avoid exposure through the skin and eyes from all reagents used. A labcoat is also recommended. Cracked, chipped or broken glassware **must not** be used. Special attention must be paid to separatory funnels. Star cracks in the separatory funnel may cause the separatory funnel to explode when pressure is created inside during shaking.

Procedure : 1.0 Organization and Set-up

1.1 Remove the samples to be extracted from the refrigerator. This set of samples and corresponding QC samples are the extraction batch. Each extraction batch must include a laboratory method blank (LMB), laboratory fortified blank (LFB), matrix spike (MS) and matrix spike duplicate (MSD) of a sample.

1.1.1 Sample volume is approximately 1L for most samples. Low level PCB samples may not be extracted with this method.

1.1.2 The LMB and LFB are approximately 1L of carbon-filtered deionized water (C-dH_2O). The LFB is a fortified spike of reagent water. Both the LMB and LFB are treated in the same manner as the samples.

1.1.3 One set of spikes, a MS and MSD, is extracted for each QC batch not exceeding 20 samples. Select a sample with 3L of sample available. Label one sample container MS and one MSD, leaving one container for the unspiked sample.

If only 2L are available, split one liter of the sample into two portions using a 500mL graduated cylinder to measure their volumes. Record the sample volumes for the spikes in the appropriate extraction lab notebook.

If none of the samples have more than 1L of sample available, do a LFB and LFB-duplicate instead of the MS and MSD.

1.2 Remove the appropriate surrogate(s) and spike(s) from the freezer as determined from the "Surrogate and Spike Chart."

1.3 Rinse one 2L separatory funnel and stopper with $MeCl_2$ for each sample after checking the separatory funnel for star cracks. Rinse one Wheaton 500mL amber bottle with $MeCl_2$ for each of the following samples which does not have an original sample container: LMB, LFB, MS, MSD.

1.4 Label the separatory funnels and amber bottles with the sample identification. Include the date and extraction type on all sample and amber containers.

2.0 Sample preparation

2.1 Check the separatory funnels to make sure the stopcocks are closed. Take the sample to the balance and tare the entire sample, jar and lid. Pour the sample into the appropriately labeled separatory funnel. Be careful not to touch inner lip of sep funnel with gloves. Immediately return to the balance and weigh the now empty sample jar. Record the negative weight reading from the balance on the bench sheet as mLs of sample. Repeat for all samples.

2.2 Check pH by dipping a disposable pipet into sample and distributing sample onto a piece of 1-14 indicator paper. Compare colors to pH chart.

2.3 Add necessary surrogate and spikes (refer to "Surrogate and Spike Chart).

2.4 Adjust pH if necessary. After adjustment record the pH measured of each sample on the extraction batch sheet.

2.4.1 Acid (A) extraction - adjust pH to less than or equal to 2 with (1:1) H_2SO_4. To make (1:1) H_2SO_4, slowly add 250mL H_2SO_4 to 250mL C-dH_2O in 1L Erlenmeyer flask. **CAUTION:** Solution will be very hot. Allow to cool before use. **NEVER** add H_2O to acid!!!

2.4.2 Base (B) extraction - adjust pH to greater than or equal to 12 with 10 N NaOH. To make 10 N NaOH, measure 200g NaOH pellets into 1L Erlenmeyer flask. Add 500mL C-dH_2O. Stir to dissolve pellets. **CAUTION:** Solution will be very hot. Allow to cool before use.

2.4.3 Neutral (N) extraction (including PCB extraction)
pH should be between 5 and 9. If pH is not in this range, adjust sample accordingly with (1:1)H_2SO_4 or 10 N NaOH.
NOTE: Each sample must have a LMB associated with it that is treated in the same manner as the sample. For example, if the pH of a sample is changed, the LMB must have the same amount of acid or base added to it.

2.4.4 ABN extraction -. Change pH to less than or equal to 2 and follow complete extraction procedure for A extraction. Adjust pH to greater than or equal to 12 and follow complete extraction procedure for B extraction. Always do A extraction before B extraction as is stated in EPA 3510C.

3.0 Extraction

3.1 Add 60mL of $MeCl_2$ to sample container from tipping dispenser. Cap container and gently swirl the sample bottle a few times in order to rinse the container sides with solvent. Carefully pour the $MeCl_2$ into the separatory funnel with the associated sample. After replacing stopper, invert sep funnel and open stopcock to relieve pressure. Open and close the stopcock repeatedly while shaking until pressure build-up is no longer observed. Shake sample for 2 minutes. Let aqueous and $MeCl_2$ layers separate for a minimum of 10 minutes. Drain $MeCl_2$ extract into sample

container. (If not available, collect extract in Wheaton 500mL amber bottle). If layers do not separate, manual techniques for separation may be necessary. The experience of the technician will be crucial in choosing one of the following techniques. If necessary, ask for direction from the supervisor.

3.1.1 Use a solvent rinsed stirring rod to break up the emulsion in the separatory funnel.

3.1.2 Filter extract through solvent rinsed glass wool.

3.1.3 Transfer extract to a centrifuge tube. Centrifuge for 5 minutes in the centrifuge located in the hazardous waste lab. Transfer contents of the centrifuge tube back to the separatory funnel and drain $MeCl_2$ extract as in 3.1.

3.2 Repeat 3.1 two more times with 60mL aliquots of $MeCl_2$ added directly to sep funnel. Combine $MeCl_2$ extracts in sample container.

3.3 Sample extracts may be stored in Teflon-lined screw cap amber bottles at 4^0C for up to 10 days before concentration.

4.0 Filtration

4.1 Rinse powder funnels containing silanized glass wool and Na_2SO_4 with ≈30mL $MeCl_2$. Rinse turbovap (TV) tubes with $MeCl_2$. Pour sample extracts through funnels into TV tubes.
NOTE: If extracts are biphasic, ask for direction. Aqueous layers must be separated from extracts before filtration as H_2O will clog filters.

4.2 Rinse ≈30mL $MeCl_2$ in sample container and pour through filter.

5.0 Concentration

5.1 Proceed to turbovap concentration SOP.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-11-00
Kent Lawrence

Supervisor: _____ Date: 10/12/00
Michael Jaeger

Laboratory Director: _____ Date: 10/12/00
Michael Jaeger

QA Approval: _____ Date: 12-Oct-2000
Pollyann Nee

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STANDARD OPERATING PROCEDURE OF ACCELERATED SOLVENT EXTRACTION (3545)

Principal References:

U.S. EPA's "Test Methods for Evaluating Solid Wastes," SW-846, 3rd Edition, Update III, December, 1996.

Application:

This procedure is used for extracting water insoluble or slightly water soluble semivolatile organic compounds from soils, clays, sediments, sludges and waste solids. The method uses elevated temperature (100°C) and pressure (1500 - 2000 psi) to achieve analyte recoveries equivalent to those from soxhlet extraction, using less solvent and taking significantly less time than the soxhlet procedure. This procedure was developed and validated on a commercially-available, automated extraction system.

This method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, which may then be analyzed by a variety of chromatographic procedures.

This method has been validated for solid matrices containing 250 to 12,500 µg/kg of semivolatile organic compounds, 250 to 2500 µg/kg of organophosphorus pesticides, 5 to 250 µg/kg of organochlorine pesticides, and 1 to 1400 µg/kg of PCBs.

Summary of Method:

Approximately 10 g of sample are mixed with approximately 5 g of diatomaceous earth, and loaded into a 30 mL extraction cell. Surrogates/spikes are added. The sample is equilibrated for 5 minutes and extracted for 6 minutes using methylene chloride at elevated temperature (95°C) and elevated pressure (1800 psi).

The extraction cell is allowed to cool to room temperature and the solvent is collected in a 60 ml glass vial.

The extract may be concentrated, if necessary, and as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed.

Interferences:

Phthalate esters found in many plastics are a major source of contamination. Therefore it is crucial that samples and reagent contact glass or Teflon only. In particular, the following precautions must be taken:

- Plastics must not be used in any part of the procedure (including plastic pipets and squirt bottles).
- Gloves or glove powder must not come in contact with any surface in which the sample or extract is exposed.
- PCB samples may be subjected to cleanup methods to remove interferences if necessary. (See SOP KO8082 for PCB Cleanup Methods).

Apparatus & Materials:

Automated Accelerated Solvent Extractor (ASE) - Dionex Accelerated Solvent Extractor with extraction cells.

Vials for collection of extracts - 60 mL, pre-cleaned, open top screw-cap with PTFE-lined silicone septum.

Analytical Balance: Mettler PM 5600 or equivalent
Glass Beakers: 250 mL pyrex
Wooden spatulas: Fisher Brand tongue depressors
Glass fiber filters: Dionex 1.91 cm GF/B
Pyrex® powder funnels
Syringes 1 mL, 100 µL
Metal spatulas, black Sharpe® black felt tip marker

Reagents:

Methylene chloride - pesticide residue grade
Acetone - pesticide residue grade
Methanol - pesticide residue grade
Nitrogen gas, high purity for purging extraction cell
Diatomaceous earth - Celite^{R} brand pesticide residue grade certified, for drying sample

Safety:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, $MeCl_2$ and PCBs are suspected human carcinogens. Solvents, samples, reagents and spiking and surrogate solutions should be treated as potential health hazards and exposure to them should be minimized. A reference file of Material Safety Data Sheets (MSDS) is available to all employees and the MSDS for each chemical used should be read prior to use. All solvents must be used in a fume hood to avoid inhaling the vapors. The hood must be operated at a safe face velocity as monitored by the velocity alarm on the hood. Gloves and safety glasses must be worn to avoid exposure through the skin and eyes from all reagents used. A lab coat is also recommended. Cracked, chipped or broken glassware must not be used.

Sample Collection, Preservation and Handling:

Sample Type	Preservation	Container	Holding time, collection to extraction	Holding time, extraction to analysis
Soil/Sediment	None; 4C∓2C	500 mL glass bottle	14 days	40 days
Waste, solid	None; 4C∓2C	500 mL glass bottle	14 days	40 days

Procedure:

Organization and Set-up:

Remove the samples to be extracted from the refrigerator. This set of samples and corresponding QC samples are the extraction batch. Each extraction batch can include up to twenty samples, and must include a Laboratory Method Blank (LMB), laboratory fortified blank (LFB), matrix spike (MS) and matrix spike duplicate (MSD) of a sample.

Sample weight extracted will be approximately 10.0 g. The LMB and LFB will consist of approximately 15.0 g of diatomaceous earth (Celite). They are treated in the same manner as the samples.

Remove the appropriate surrogate(s) and spike(s) from the freezer as determined from the Surrogate and Spike Chart (See Table I).

For each sample to be extracted, rinse a clean dry, 250 mL Pyrex beaker three times with methylene chloride. Allow the beakers to air dry in the hood.

Sample Preparation:

Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks. See KAR SOP KG462 for specific procedure for percent solids determination.

Grind or otherwise reduce the particle size of the waste so that it is free flowing. Sufficient mixing or grinding can be accomplished using ether a wooden tongue depressor or a metal spatula. If a metal spatula is used it must be decontaminated between samples by washing with soap and water, followed by acetone and methylene chloride rinses.

Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

Place a rinsed beaker on the balance and TARE (this will reset the scale to 0.0 g, accounting for the weight of the beaker).

Weigh approximately 10.0 ± 0.1 g of prepared sample into one of the prepared beakers using a wooden tongue depressor. Record the exact weight of sample used on the Extraction Batch Data Sheet. Tare beaker with sample. Weigh approximately 5.0 ± 0.5 g Celite^R into the beaker. Record the exact weight on the Extraction Sheet. Slightly more (+1.0 g), or less (-1.0 g) to Celite^R may be used depending on how much moisture is in the sample. The purpose is to produce a free flowing sample that is as dry as possible. Stir the sample and Celite^R together (using the same wooden tongue depressor used to weigh the sample) until both are free flowing and well mixed.

Place a 1.91 cm glass fiber filter in the bottom a clean, methylene chloride rinsed cell. Transfer the sample from the beaker to the cell with the aid of a pyrex glass powder funnel. If only one funnel is used, it must be washed and solvent rinsed between samples according to the same

procedure used on the metal spatula.

Using the appropriate volume gas tight syringe (See Table 1) add surrogate(s) to sample. Refer to Table I, Surrogate and Spike Chart, for exact volume to add.

If the sample is a MS, MSD, or LFB, add the appropriate spike(s) in the same manner as the surrogate. Refer to Table I, Surrogate and Spike Chart.

Immediately cap the cell and place it in position on the ASE unit. Take a 60 mL glass vial with PTFE lined screw cap and label it with the sample ID using a sharpe marker. Place the labeled vial in the corresponding position to the cell on the ASE unit.

Repeat the process for each sample, MS and MSD.

Repeat the process for the LMB and LFB substituting 15 ± 0.5 g of Celite^{R} for the sample.

ASE Extraction Conditions:

Oven temperature:	95^{0}
Pressure:	1800 psi
Static time:	6 min (after 5 min preheat equilibration)
Flush volume:	60% of the cell volume
Nitrogen purge:	180 seconds @ 150 psi

Extract Samples:

Turn on the Nitrogen gas for the ASE unit. Regulator pressure should be 150 - 180 psi.

Make sure the 2 L solvent bottle is at least ½ full. If not, refill with methylene chloride.

Check the purge vial for waste, emptying it if it is ½ full or more.

Empty the three rinse vials of waste solvent and replace the PTFE lined septa.

Turn on the power to the ASE unit. Press the **RINSE BUTTON**, this will perform an initial rinse of the system.

Load Method 1 and the appropriate starting vial number. Press **START**. Each sample extraction will take approximately 15 minutes. Allow the extracts to cool after completion. Place cooled extracts in the refrigerator until cleanup, concentration, or analysis is performed (See the appropriate KAR SOP).

Routine Preventative Maintenance:

Routine maintenance procedure for the ASE unit include:

Emptying and washing the cells and caps of spent soil/celite samples. Filling the solvent reservoir as needed, and emptying the waste vials as needed. Also, watch for leaks from the solvent reservoir, pumps, and valves.

Periodic maintenance on the ASE unit consists of:

Replacing the cell caps external o-rings (P/N 049457) every 50 to 75 extractions, or when worn. Replace the PEEK seals (P/N 049455) inside all caps after 50 - 75 extractions.

Quality Control:

Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference - free. This is accomplished through the analysis of a solid matrix method blank (e.g., clean Celite^{R}). Each time samples are extracted or when there is a change in reagents, a method blank needs to be extracted and analyzed for the compounds of interest. The method blank should be carried through all stages of the sample preparation and measurement.

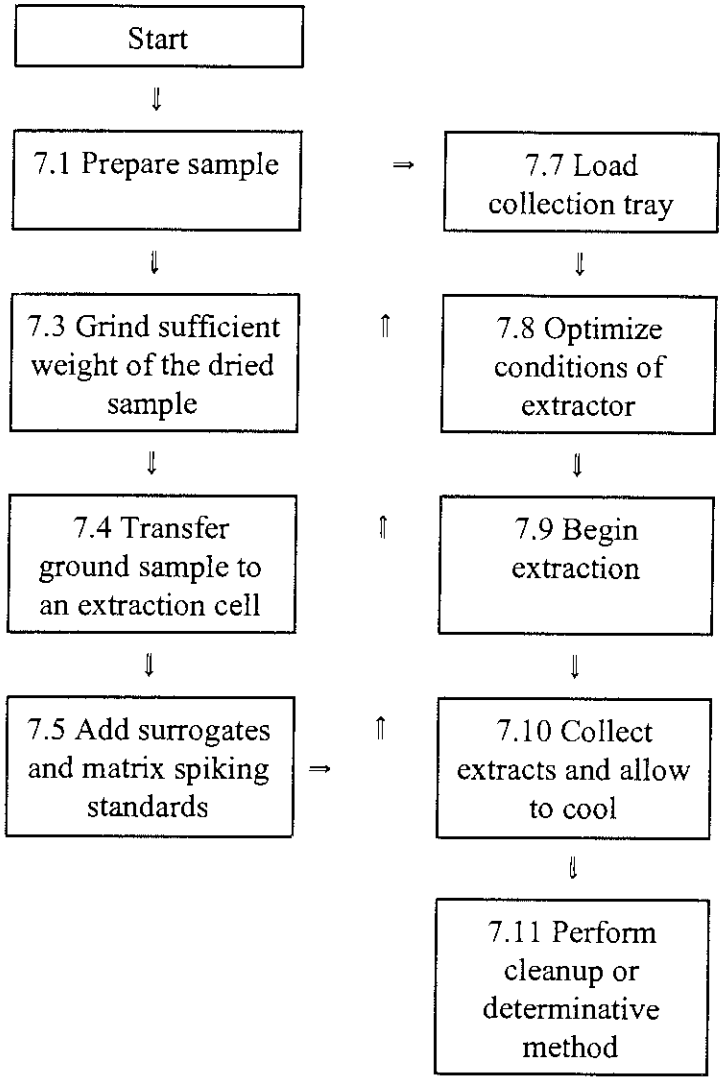
A matrix spike/matrix spike duplicate and a laboratory Fortified Blank will also be prepared and analyzed with each batch of samples prepared by this procedure.

Table 1: Surrogate and Spike Chart

Sample Type and Method*	Surrogate Solution			Spike Solution			Extract Final Volume (mL)
	Conc.* (µg/mL)	Amount to add to sample	Syringe to use	Conc.* (µg/mL)	Amount to add to sample	Syringe to use	
Aldehdes by KO8315 (Aqueous, Soil)	---	None		1000	25 µL	100 µL	10.0
BNpH by KO8270 (Aqueous, Soil)	500	100 µL	250 µL	1000	50 µL	100 µL	1.0
Acid pH by KO8270 (Aqueous, Soil)	1000	50 µL	100 µL	2000	25 µL	100 µL	1.0
BNpH by KO8270 (Waste, Oil)	500	1.0 mL	2 mL	1000	500 µL	1 mL	10.0
Acid pH by KO8270 (Waste, Oil)	1000	500 µL	1 mL	2000	250 µL	1 mL	10.0
PCB by KO8082 (Aqueous, Low Level Soil)	2	100 µL	250 µL	2	100 µL	250 µL	1.0
PCB by KO8082 (Soil)	20	100 µL	250 µL	10	500 µL	1 mL	10.0
PCB by KO8082 (Waste, Oil)	20	100 µL	250 µL	100	125 µL	250 µL	5.0
Herbicides by KO8151 (Aqueous, Soil)	50	100 µL	250 µL	5	100 µL	250 µL	1.0
Pesticides by KO8081 (Aqueous)	2	100 µL	250 µL	2-5	100 µL	250 µL	1.0
Pesticides by KO8081 (Soil)	20	100 µL	250 µL	2-5	1 mL	2 mL	10.0

***Analytical SOP details the preparation of these surrogate and/or spike solutions**

Method 3545
ACCELERATED SOLVENT EXTRACTION



Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: _____ Date: 10-10-00
Kent Lawrence

Supervisor: _____ Date: 10/12/00
Michael Jaeger

Laboratory Director: _____ Date: 10/12/00
Michael Jaeger

QA Approval: _____ Date: 12-Oct-2000
Pollyann Nee

Method: KO3500B
Date: 5/93
Date Revised: 6/6/98

STANDARD OPERATING PROCEDURE FOR Turbovap Concentration

Principal References:

"Turbovap Concentrator Operator's Manual," Zymark Corporation, 11/19/91.

EPA, "Test Methods for Evaluating Solid Wastes," SW-846, 3rd Edition, Update III, Method 3500B: Organic Extraction and Sample Preparation, U.S. EPA Office of Solid Waste and Emergency Response, Washington DC., December, 1996.

Application:

This procedure is a method for concentration of solvent extracts produced from separatory funnel extraction SOP (KO3510), solid phase extraction SOP (KO3535) and accelerated solvent extraction SOP (KO3545).

Summary of Method:

The Turbovap (TV) concentration workstation provides automated sample evaporation using a gas vortex shearing action to maintain high evaporation rates. A "helical flow," created by the stream of nitrogen directed into each sample, sets up a vortexing action that provides for sample homogeneity and continuous rinsing of the tube wall.

Safety:

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, dichloromethane and PCBs are suspected human carcinogens. Solvents and sample extracts should be treated as potential health hazards and exposure to them should be minimized. A reference file of Material Safety Data Sheets (MSDS) is available to all employees and the MSDS for each chemical used should be read prior to use. All solvents must be used in a fume hood to avoid inhaling the vapor. The hood must be operated at a safe face velocity as monitored by the velocity alarm on the hood. Never operate the turbovap units without the TV exhaust hoses placed in a fume hood. Gloves and safety glasses must be worn to avoid exposure through the skin and eyes from all reagents used. A labcoat is also recommended. Cracked, chipped or broken glassware must not be used.

Caution: Do not concentrate ethyl ether or MTBE to dryness as explosion may result.

Apparatus, Materials and Reagents:

- Turbovaps (TV) #1, #2, #3, #4; all Zymark TV II models except #1=TV1
- 300 mL Turbovap concentration tubes with 1.0 mL calibration marks
- Pyrex powder funnels
- Glass wool, silanized
- Sodium sulfate, granular, 10-60 mesh, pesticide residue grade
- Methylene chloride, pesticide residue grade
- Hexane, pesticide residue grade
- Acetone, pesticide residue grade
- Turbovap tube racks
- Autosampler vials, 1.5mL with PFTE-lined crimp caps
- Crimper
- Disposable Pasteur pipettes, 9"
- Pipette bulb
- Sharpe® marker

Procedure:

1.0 Organization and Set-up

1.1 For each sample to be concentrated, prepare a TV tube, a powder funnel with a small plug of glass wool and approximately 15 grams of sodium sulfate, and an autosampler vial with cap.

1.2 Rinse the sodium sulfate/funnels with approximately 10-20mL of methylene chloride and allow to air dry in hood. Rinse the TV tubes three times each with methylene chloride and allow to dry upside down in racks in hood.

1.3 Using a Sharpe® marker, label enough pre-calibrated autosampler vials for all the sample extracts being concentrated with the appropriate sample number and analysis to be performed. There should be enough space on the LFB, LMB, MS and MSD labels to also include the extraction date.

1.4 TV Water bath level - Fill with deionized water so that the water bath level will be higher than the solvent level in the TV tubes. (In addition, water in bath must be changed monthly. Refer to maintenance section for procedure).

1.5 Nitrogen supply - Check nitrogen supply and turn on the main N_2 value in the gas storage room. Turn the N_2 control knob on the hood approximately ¼ turn counterclockwise (on).

1.6 Turn on power to TV workstations.

1.7 Set TV to the following settings:

CONTROL BOARD SETTINGS

TV#2	Solvent - 0 (all positions)
	Dry - NO (all positions)
TV #1, TV#3, TV#4	Endpoint select - sensor
	Bath temp - 40°C to 50°C
	Endpoint time - 0

1.8 For most situations, Turbovap workstations are set above the boiling point of the solvent being used because the nitrogen has a cooling effect on the surface of the solvent. See Table 1 for specific solvent temperatures and pressures.

Table I. Turbovap Temperature Pressure Settings

Solvent	Temperature	Pressure	
		start	end
Methylene chloride	**40°C**	**15psi**	**20psi**
Ethyl ether	**40°C**	**15psi**	**20psi**
Hexane	**50°C**	**15psi**	**20psi**
Methanol	**50°C**	**15psi**	**20psi**

2.0 Concentration

2.1 Dry each sample extract by passing it through the solvent-rinsed sodium sulfate/funnel and into the TV tube. Rinse the sample bottle two times with methylene chloride, decanting it into the funnel/TV tube after each rinse. Thoroughly rinse the sodium sulfate/glass wool with methylene chloride into the TV tube so as to pass any residual sample components into the TV tube. The

sample extracts are now ready for concentration.

2.2 After the water bath has warmed to the proper temperature, carefully insert TV tubes into position. (**WARNING:** The reservoir tips of the TV tubes are very fragile, handle with caution. If a TV tube breaks and the $MeCl_2$ extract gets into water bath, remove all TV tubes immediately. Lift rack from water bath after unscrewing center bolt. Drain and clean water bath immediately.)

2.3 When all tubes are in position, lower TV cover.

2.4 Turn N_2 supply on at the hood.

2.5 TV#2: At regulator, adjust N_2 pressure so that a vortexing action is created in each tube.

TV#1, TV#3, TV#4: Press start control for each position in use. Adjust N_2 pressure using the pressure regulator located on the lower left side of TV so that a vortexing action is created in each tube.

Do not raise the N_2 pressure too high, in order to prevent splashing. Ideally, pressure should be between 10-20 psi; however, when extracts contain greater than 200mL, a pressure less than 8 psi (≈4-6 psi) may be necessary. As sample extracts concentrate, check intermittently and adjust N_2 pressure as high as possible (up to 20 psi) to maintain the vortexing action.

2.6 When sample extracts have concentrated to ≈2mL, the following procedures may be performed if necessary.

2.6.1 Solvent exchange

2.6.1.1 PCB/Pesticide extracts require the addition of ≈30mL hexane.

2.6.1.2 Sonication extracts require the addition of 30mL $MeCl_2$.

2.6.1.3 Formaldehyde extracts require the addition of 30 mL methanol.

In all cases of solvent exchange, the sample/solvent mixture should be hand-swirled in the TV tube after the exchanging solvent is added to facilitate mixing.

Note: If the original sample extract exceeded 200mL, add additional amounts of sample extract which require concentration. This will always be the case for extracts from continuous liquid-liquid extraction. Use the same funnel as previously used to add sample extract to TV tube.

2.7 Concentrate sample extracts to no less than 0.5mL. Do not concentrate sample extracts to dryness or irreversible loss of sample components may occur. If any extract goes to dryness, it must be re-extracted and/or flagged as estimated result. CONCENTRATION OF ETHYL ETHER OR MTBE TO DRYNESS MAY RESULT IN EXPLOSION. Remove TV tubes from TV.

Procedure cont'd :

3.0 Final Extract Transfer

3.1 Hold the Turbovap tube within the line of sight.

3.2 Using a 9" disposable Pasteur pipette, add enough fresh solvent to bring the sample to the 1mL mark by rinsing down the side walls of the tube in a swirling motion at the point just above where the tube narrows.

3.3 Take the entire 1mL sample into the pipette and rinse the same lower portion of the Turbovap tube.

3.4 Repeat the above technique two more times. At this point, the extract will have evaporated to about 0.5 mL.

3.5 Repeat step 3.2 with fresh solvent and bring to the final 1mL mark.

3.6 Using the same pipette, the 1mL sample extract is now ready for transfer to an autosampler vial. (If 1mL is not the final endpoint, perform a quantitative transfer. See Table II for appropriate final volumes.)

Table II. Final volumes and solvents for Turbovap concentration

Method	Aqueous	Soil	Sludge (<5% solids)
EPA 8270C Acid, base/neutral extractables by GC/MS	Final volume = 1.0 mL solvent = $MeCl_2$	Final volume = 1.0 mL solvent = $MeCl_2$	Final volume = 1.0 mL solvent = $MeCl_2$
EPA 8081/8082 Pesticides and PCBs by GC/ECD	Final volume = 1.0 mL solvent = Hexane	Final volume = 10.0 mL solvent = Hexane	Final volume = 5.0 mL solvent = Hexane

3.7 Sample extract is now ready for additional cleanup or analysis. Refer to appropriate SOP.

4.0 Shutting down

4.1 Store TV with cover in the up position to prevent moisture from accumulating on the inside cover.

4.2 Replace the plastic caps which cover the TV tube positions in the water bath.

4.3 Turn N_2 regulators to the lowest flow position.

4.4 Turn off N_2 supply at the hood and at the N_2 tank in the gas storage room.

4.5 Turn off the power to the TV units.

4.6 Store sample extracts in designated vial file storage unit and record the final volume and file location in appropriate logbook.

Maintenance:

Monthly - Since turbid water may affect sensor operation, the water in the water bath must be replaced monthly. Using the water bath siphon pump, empty the water from the bath. Fill the bath with deionized water until the water level is approximately 1 inch from the top. Add 15 drops of Clear Bath, a biological growth retardant. Use the bubble dislodger to dislodge bubbles from the sensors. Occasionally, remove the rack from

the bath after unscrewing the center bolt and clean the bath walls. Record all maintenance in the logbook corresponding to the appropriate turbovap.

Quarterly - Perform cell diagnostics per the manual instructions to test sensors, switches, lights, gas pressure and valves. Replace sensors and/or switches when necessary. Record all maintenance in the logbook corresponding to the appropriate turbovap.

KAR LABORATORIES, INC.

PREVENTIVE MAINTENANCE PROCEDURES

PREVENTATIVE MAINTENANCE

INSTRUMENT	MAINTENANCE PROCEDURES / SCHEDULE	SPARE PARTS IN STOCK
Milton-Roy Spectronic 21D UV/Vis Spectrophotometer	1. Keep all surfaces clean and dry (daily). 2. Inspect exposed metal parts for corrosion every year. 3. Clean cuvettes as needed.	1. Tungsten lamps (2) 2. Cuvettes (1, 2.5, 5cm)
Hewlett-Packard 4500 ICP/MS	1. Tune and calibrate daily. 2. Clean filters every six months. 3. Comprehensive preventative maintenance service performed by HP field engineer twice annually.	1. One-year supply of all consumables 2. Electron multiplier 3. Full service contract
Finnigan ITS 40 GC/MS	1. Tune and calibrate daily. 2. Check foreline pump oil level weekly. 3. Check (refill) calibration vial every three months 4. Replace foreline pump oil every three months. 5. Replace turbo pump oil every six months. 6. Clean ion trap as needed. 7. Replace filaments as needed. 8. Replace electron multiplier as needed. 9. Replace septa injector port inserts/clip column as needed. 10. Replace column as needed. 11. Clean fan filters/dust boards annually.	1. Foreline pump oil 2. Turbo pump oil 3. Filaments 4. Electron multiplier 5. Chromatography columns 6. Septa 7. Injector port inserts
Hewlett Packard 5890/5972 GC/MS	1. Tune and calibrate daily. 2. Check foreline pump oil level weekly. 3. Check (refill) calibration vial every three weeks. 4. Replace foreline pump oil every six months. 5. Replace foreline trap pellets every six months. 6. Check (replace) diffusion pump oil every year. 7. Clean ion source as needed. 8. Replace filaments as needed. 9. Replace electron multiplier as needed.	1. Foreline pump oil 2. Diffusion pump oil 3. Filaments 4. Electron multiplier 5. Chromatography columns 6. Septa 7. Injector port inserts
Tremetrics 9001 dual ECDs	1. Degradation check and calibration daily. 2. Replace liner and septa as needed. 3. Replace clip guard column as needed. 4. Replace analytical columns as needed. 5. Check (re-adjust) saturation current monthly.	1. Injector port liners 2. Septa 3. Guard column 4. Analytical columns

PREVENTATIVE MAINTENANCE

INSTRUMENT	MAINTENANCE PROCEDURES / SCHEDULE	SPARE PARTS IN STOCK
Hewlett Packard 4500 ICP-MS	1. Tune and calibrate daily. 2. Clean filters and lenses every six months. 3. Change sampler and skimmer cones as needed. 4. Change vacuum oil every six months. 5. Change rinse solutions daily. 6. Change water cooler water every six months.	1. Full service contract. 2. One year supply of all consumables
Applied Research Laboratories 3560 ICP-AES	1. Profile and calibrate daily. 2. Clean filters every six months. 3. Change pump tubing daily. 4. Change vacuum oil every six months. 5. Replace PA tube when needed. 6. Change rinse solution daily.	1. Pump tubing 2. PA tube 3. Spray chamber 4. Torch assembly 5. Nebulizer 6. RF coil
Perkin Elmer 3000XL ICP-AES	1. Tune and calibrate daily. 2. Change pump tubing daily. 3. Change water cooler water every six months. 4. Change rinse solutions daily. 5. Clean filters every six months.	1. Pump tubing 2. Spray chamber 3. Torch assembly 4. Nebulizer 5. RF coil
Varian AA-20 w/ VGA-76 Cold Vapor Generator (Hg only)	1. Optimize and calibrate daily. 2. Change pump tubing daily. 3. Release gas pressure when completed.	1. Hg lamp 2. Pump tubing 3. Flow cell 4. Gas liquid separator 5. Mixing cell

KAR LABORATORIES, INC.

INSPECTION/ACCEPTANCE REQUIREMENTS

FOR SUPPLIES AND CONSUMABLES

AUTHORIZED COPY

SOP No.: KG066.01
Date issued: 11/16/00
Next revision due: 11/01

STANDARD OPERATING PROCEDURE

Handling, Labeling and Assigning Expiration Dates to Chemicals and Consumables

1.0 Principal References

1.1 *KAR Laboratories, Inc. Quality Assurance Manual*, KAR Laboratories, Inc.
1.2 *Catalog Handbook of Fine Chemicals*, Aldrich Chemical Co.

2.0 Scope and Application

2.1 This procedure applies to all chemicals and consumables received at KAR Laboratories.

3.0 Summary of Procedure

3.1 The purchase of reagents, solvents and consumables is controlled at each laboratory through a purchase order system that includes management approval. Management and QA define the appropriate grade needed for each laboratory, thus maintaining the quality of the materials.

3.2 All chemicals stored/used at KAR Laboratories must be handled cautiously for safety reasons and properly labeled with the chemical name, date received, expiration date and date opened.

3.3 An expiration date is assigned by KAR Laboratories to all chemicals received without a manufacturer's expiration date. The date assigned is based on the chemical vulnerability of the material as indicated in the Aldrich Handbook.

3.4 Chemicals should remain at an approved storage location until ready for use and returned to storage as soon as possible. Storing chemicals, reagents or solutions in the laboratory hood is not recommended.

3.5 Chemicals are purchased from reputable sources and have approved, filed MSDSs (Material Safety Data Sheets). Certificates of Analysis are available documenting purity and contaminants. If a chemical does not have suitable characterization, testing will be performed in house or the chemical will not be used when it could potentially affect assay results and sample integrity.

3.6 Many laboratory supplies are in the form of consumables, that is, items that are intended to be used once and discarded. Consumables are purchased from a reputable source and meet manufacturer's strict requirements for integrity. KAR Laboratories ensures that any consumable used during sample processing does not adversely contribute to an assay result. If a consumable is suspect, tests will be performed to ascertain any source of contamination. Pre-washing may be necessary for certain consumables, including filters, sorbents, glass wool, etc. Any such requirement will be specified in the appropriate laboratory SOP. KAR Laboratories utilizes reagent blanks and check samples during all analysis to ensure that any contamination from chemicals, consumables and laboratory glassware/equipment is detected.

4.0 Equipment

4.1 Waterproof marker

4.2 *Catalog Handbook of Fine Chemicals*, Aldrich Chemical Co.

5.0 Procedure

5.1 Remove the container from its transportation packaging and determine whether the manufacturer has assigned an expiration date. Chemicals already having a manufacturer's expiration date assigned are dated, initialed and shelved according to KAR's QA/QC policy. Labels must be legible and indicate the chemical name.

5.2 All other chemicals are dated, initialed and assigned an expiration date using a fine-point, waterproof marker making sure the label clearly indicates the chemical name.

5.2.1 Look up the chemical compound in *Catalog Handbook of Fine Chemicals* (Aldrich). If the manual indicates that the compound is hygroscopic, light-sensitive, moisture-sensitive or deliquescent, assign an expiration date of five years added to the received date provided that it can be stored appropriately.

5.2.2 Unless the chemical is known by some other reliable reference to fall into one of the categories listed in 5.2.1 or have a shelf-life of less than five years, assign an expiration date of ten years added to the received date to all other chemicals.

5.3 Because these expiration dates have been arrived at arbitrarily, any chemical exceeding an expiration date not assigned by the manufacturer may still be used if it can be shown analytically to be of sufficient potency or purity so as not to adversely affect the outcome of an analysis.

5.4 If a chemical is close to its assigned expiration date, management should be

notified to determine if the expiration date can be extended or if a new supply should be ordered.

5.5 All containers used for sampling are single use, pre-cleaned and certified. For each lot of containers, the distributor certifies that no CLP Contract Required Detection Limit (CRDL) is exceeded for any measured compound, element or ion.

5.5.1 Representative containers from each lot are analyzed by the distributor for volatile and semi-volatile organic compounds by GC/MS. Containers are also analyzed for chlorinated pesticides and PCBs by GC-EC, for trace metals by either atomic absorption or atomic emission spectrometry and for certain anions by ion chromatography. Each successful analysis of a non-contaminated field blank confirms the container's cleanliness.

6.0 QA/QC Requirements

6.1 All analysts using any chemical for an analysis are required to determine whether that chemical has exceeded its expiration date. Any chemical which has exceeded a manufacturer's expiration date may not be used for the analysis. Any chemical exceeding an arbitrary expiration date may only be used according to section 5.3.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: David R. Alkema Date: 11/16/00
Dave Alkema

Supervisor: Michael Jaeger Date: 11/16/00
Michael Jaeger

Laboratory Director: Michael Jaeger Date: 11/16/00
Michael Jaeger

QA Approval: Pollyann Nee Date: 16-Nov-2000
Pollyann Nee

4. LABORATORY SUPPLIES, CHEMICALS AND EQUIPMENT

4.1 Laboratory Glassware

4.1.1 **Specifications.** Glassware, chemicals and equipment used at KAR Laboratories are selected to conform to the specifications defined in the method of analysis. Items not specifically mentioned in a particular method of analysis should conform to good laboratory practices. For example, Class A volumetric glassware is used for all measurements which require a volume determination. If an item is available in a disposable configuration, then that option is sometimes preferred to avoid cross-contamination or introduction of other contaminants to a sample. Once it has been established that a particular supplier or manufacturer has a good record of supplying an item of suitable utility, ordering that item from a different source should be avoided.

4.1.2 **Calibration Checks.** All repeating pipetters are calibrated weekly and balances are calibrated daily.

4.1.3 **Cleaning Procedures**

4.1.3.1 General labware-washing will include (at a minimum) a detergent wash in hot water, three rinses with tap water, and three rinses with ASTM Type II reagent water. The labware is then inverted and suspended by external means to dry.

4.1.3.2 Labware for trace metals analysis - includes a detergent wash in hot water, three tap water rinses, one rinse with 1:1 nitric acid, one rinse with 1:1 hydrochloric acid, followed by three rinses with ASTM Type II reagent water. The labware is stoppered and stored wet.

4.1.3.3 Purgeable hydrocarbon labware - consists of cleaning as outlined in 4.1.3.1 with a final baking at 105 degrees C for a minimum of two hours.

4.1.3.4 Pesticides and acid/base-neutral extractables labware - incorporates the cleaning outlined in 4.1.3.1 followed by one rinse using pesticide-grade acetone and one rinse using pesticide-grade hexane. The containers are then inverted and suspended by external support to dry.

4.1.3.5 In all cases the sample bottle cleaning recommendations of the appropriate method and/or SOP should be followed.

4.1.4 **Testing for Contamination.** Contamination is monitored on a routine basis by the analysis of Laboratory Method Blanks (LMB). Reagent water is carried through all steps of an analysis parallel to the samples being analyzed. In this manner, any laboratory-born contamination introduced by reagents, glassware or utensils should be obvious, since any level of analyte above the method detection limit present in the LMB suggests contamination. A systematic trouble-shooting scheme may then be implemented, with any new or different variable being the most likely suspect.

The LMB is used throughout the laboratory. Most wet chemical methods include a LMB as part of the Standard Operating Procedure. Organic instrumental analysis includes a LMB after every calibration standard, and also as a means of verification that sample component carry-over from a previous high-level sample has not occurred.

4.1.5 **Storage.** KAR Laboratories has adequate storage capability and therefore has greater flexibility in providing an appropriate environment for special applications. Labware for everyday use is stored on shelves at a location isolated from potential contaminants. Specially cleaned labware such as those designated for the Organic Laboratory are stored separately in the Organic Prep Lab in a covered enclosure. Labware designated for trace metals analysis are stored in the Trace Metals Laboratory in a covered cabinet to avoid potential dust contamination. Light, heat, and/or moisture sensitive items are stored in a special room intended for this use. Other items not demanding any special storage considerations are stored to provide the most efficient retrieval of the item.

4.2 Chemicals and Reagents

4.2.1 **Purity Specifications.** All chemical reagents and gases are selected to meet or exceed the specifications defined in the method of analysis.

4.2.2 **Receipt procedures.** All chemicals, reagents, gases, and other expendables must be labeled upon receipt with the date received. Upon opening the date must be recorded on the label.

4.2.3 **Shelf Life.** Many reagents have a limited shelf life. Supplies of this nature will be labeled with the date the reagent was prepared and the name or initials of the analyst who prepared it. Some laboratory Standard Operating Procedures require that associated reagents be prepared fresh daily. Other reagents such as prepared standard solutions and calibration compounds for atomic absorption and gas chromatography are

replaced on an expiration basis. If an expiration date is known when opening a new reagent, that expiration date must be recorded on the container. In no case may a calibration standard be used after 1 year has elapsed. In most cases a 6 month, 1 month or shorter expiration date is required. The appropriate SOP or method guidelines must always be followed.

4.2.4 **Laboratory Reagent Water.** ASTM Type II reagent water (also called RO and DI water) is supplied by an on-site Reverse Osmosis system with an on-demand high capacity storage tank. This system is centrally plumbed to provide reagent water to all laboratories. Reagent water purity (conductivity) is continuously monitored and recorded daily. Monthly, all common parameters including organics, trace metals, general water quality parameters and microbiology are analyzed. If the concentration of any contaminant approaches the laboratory's reporting limits, reporting of that parameter to external clients must be suspended until the problem is corrected.

4.2.5 To document traceability of chemicals and reagents, the manufacture and lot number of the item used is recorded as part of the laboratory assay preparation documentation.

KAR LABORATORIES, INC.

DATA REDUCTION, VALIDATION, AND REPORTING

STANDARD OPERATING PROCEDURE

Data Reduction, Validation and Reporting

Principal References : *Quality Assurance Manual*, KAR Laboratories, Inc.

Application :This SOP addresses the general procedures followed by laboratory personnel to ensure accuracy in sample login and the analysis, peer-review and reporting of analytical results.

Summary of Method : Samples are logged in immediately after receipt, and the Senior Project Manager reviews all project login documentation for completeness and accuracy. Analysts perform all analyses according to established methods and parameter-specific SOPs. The data is analyzed by the analyst who generated it. All data meeting the acceptance criteria specified in the parameter-specific SOP is entered into the LIMS system after going through various levels of peer-review and data entry verification. A draft report is reviewed and validated by the Laboratory Director. A final report is printed, copied and sent to the client. All final report copies are filed and stored for a period of seven years or as specified by the client.

Discussion : A number of Quality Control techniques are described in various laboratory standard operating procedures or in certain sections of the Quality Assurance Manual. These QC techniques include many practices related to the preparation and analysis of environmental samples which are designed to maximize accuracy and precision, and verify that laboratory results obtained for a specific sample reflect the true chemical composition of that sample. While these QC measures generally provide lab personnel (and our clients) with a high degree of confidence regarding the data we produce, no strategy for consistently reporting valid laboratory results is infallible. Human error associated with sample login or subsequent data entry or report generation can undermine an otherwise well-designed Quality Assurance Program if an adequate review policy does not exist.

A formal data review policy complements other Quality Control practices to ensure that the laboratory produces analytical reports of a consistently high quality. The aspects of data review which this policy addresses include the examination of results by the analyst responsible for their generation, review by qualified peer scientists or the department supervisor, and by Quality Assurance (QA). The final report review is performed by QA and either a supervisor or the Laboratory Director. The type of data being reviewed determines which personnel are responsible and what form the review takes. In addition to analytical results, other data which may require some form of review include detection limit and turnaround time requirements and other (client-supplied) project objectives which are entered to the Laboratory Information Management System (LIMS) by laboratory personnel in the Client Services Department.

Where possible, checklists are used to expedite and document the review process; data review checklists are required for all Level 4 projects.

Procedures : Project Login Peer-review (Project Manager or designee)

1. Review all login documentation according to the KAR Login QA/QC Checklist (appended).
2. Take all necessary corrective action for any discrepancies discovered.
3. Initial and date the checklist document, and place all paperwork in the active project files in numerical order according to KAR project number.

Data Reduction and Reporting (Analyst)

1. Perform all analyses according to laboratory SOPs. All raw data must record at a minimum:
   - the parameter
   - the date of the analysis
   - the analyst
   - verification of calibration
   - KAR sample identification
   - raw sample data including all requisite QC
   - final result to be reported
   - notations of results requiring qualification
2. Analyze and reduce raw data to a final result according to the parameter-specific SOP. The results of all QC samples analyzed in an analytical batch must meet the acceptance criteria specified in the SOP before sample results may be considered valid.
3. All analysts must perform an initial review of their own work.
4. Submit reportable data to a qualified analyst for review according to lab-specific protocols.

Peer-review (Qualified Analyst)

1. At a minimum, the reviewing analyst must check that the data includes the following:
   - date of analysis
   - analyst
   - parameter(s) analyzed
   - valid calibration or verification of valid calibration
   - KAR sample number
   - accurate math in all calculations
   - acceptable QC results for all blanks, spikes, dups and check standards
   - result to be reported
   - correct units
   - any condition codes needed
2. Note all necessary corrections in writing; date and initial that review was performed.
3. Return data to analyst for correction and review by departmental supervisor.

Supervisor Review (Departmental Supervisor or designee)

1. The supervisor must check that:
   - complete and accurate peer-review was performed by a qualified analyst
   - acceptance criteria have been met for valid calibration
   - requisite QC was performed
   - QC results fall within acceptable ranges
   - discrepancies noted in peer-review have been properly corrected
2. Note all necessary corrections in writing and review with analyst.
3. Return data for entry of results into LIMS by analyst.
4. Verify that data has been entered correctly into LIMS.
5. Date and initial that supervisor review was performed.

Data Validation and Final Reporting (Laboratory Director)

1. Print a draft report for final review and validation.
2. Review all client instructions and compare to lab-generated documents for compliance.
3. Review all project information and analytical results for technical accuracy and completeness (see tables below for summary of various levels of review).
4. With rare exceptions, all reports must include the following correct information:

- KAR's project number
- the client's name and address
- the client's project manager
- the client's project description
- the client's purchase order number
- copies of the chain-of-custody and all relevant project documents
- the client's sample identification
- KAR's sample identification
- the parameters requested
- the analytical results obtained
- the result units
- the analyst's initials
- the date of analysis
- the method performed
- any applicable condition codes
- KAR's invoice

5. Review all text for correct spelling, grammar and punctuation.
6. Review all data for internal consistency. Check the ion balance data which accompanies all draft reports where such data is available.
7. Review the Potential Problem report which accompanies all projects where violations have been detected by LIMS.
8. Review the Project Change Log report which accompanies all projects where changes have been entered into the LIMS.
9. Review all data with past database results (for ongoing monitoring projects only).
10. Review the invoice for correctness.
11. Submit all errors or suspected errors to the appropriate lab manager for investigation and, if necessary, correction.
12. Validate all projects meeting these acceptance criteria.
13. Print the final report and send hardcopy by U.S. Postal Service; send fax or phone verbal results as requested by client. See summary tables of data review and validation (attached).

Release of Laboratory Results Prior to Validation

1. Under certain circumstances, clients request that the laboratory release results that have not yet been subjected to the review and validation processes described earlier in this SOP. Although KAR Laboratories will usually attempt to satisfy such requests, the complete validation process must still be performed prior to the issuance of KAR's final written report. The release of pre-validated data is most often required in association with the following types of projects:
   -Emergency response field activities
   -Monthly projects with results which exceed the client's discharge limit
   -Other projects where results exceed a client's regulatory limit or other defined threshold

2. A client request for pre-validated data is often received (at some time between project initiation and the due date) via a phone call to a KAR Client Services representative or a member of the office staff. Complying with any such request is contingent upon approval from either the President, Laboratory Director, or Client Services Supervisor. Such authorization will not be granted prior to review of the preliminary results to be released. Written documentation of the authorization will be attached to the project record.

3. Alternately, the use of KAR's "Auto-notification" feature establishes, at the time of project initiation, a potential need to report pre-validated data. Since (as the name implies) this is an automatic function, no management approval is required prior to data release. A disclaimer which is provided with the results being reported will identify them as "PRELIMINARY AND SUBJECT TO CHANGE WITHOUT NOTICE" pending formal review and validation.

4. Following any release of pre-validated results, KAR's standard review/validation process must be completed before the final report is issued.

Data Storage

1. Keep all raw data documents in the short-term storage area designated in each lab area. File all notebooks, logs, benchsheets and data files chronologically by project number, breaking down according to parameter and/or client as appropriate.
2. When short-term space runs low, transfer data to long-term storage. Only KAR employees are permitted access to stored data.
3. All data and project documents are retained for seven years and destroyed at the end of the seventh year. Other retention practices may be specified by the client.
4. All data stored in the LIMS computer system is backed up on tape daily and stored off-site for a period of seven years.

A summary of all data review and validation follows:

1. Review of client instructions and comparison to laboratory-generated documents

Responsible Party	Requirement
Sample Receiving Technician	Document all communication with client on PCL Log-in project properly; DQOs and required analyses, detection limits & turnaround times understood & properly communicated to lab; draft invoice produced & checked for accuracy; use of KAR Login QA/QC Checklist required; make corrections and forward to Project Manager (or designee)
Client Services Manager	Confirm that project has been logged-in properly by Sample Receiving Technician (perform or delegate review)
Analyst	Report any apparent problems to supervisor
Peer Scientist	Report any obvious problems
Department Supervisor	Work with Client Services Dept. in the event that corrective action is necessary
Laboratory Director	Confirm that all necessary data review has been performed by appropriate personnel

2. **Review of analytical results for technical accuracy and completeness**

Responsible Party	Requirement
Client Services Dept.	Review field notes, measurements and calculations (e.g., static well elevation, pH, conductivity, dissolved oxygen, etc.).
Analyst	Document existence of valid calibration and QC data (matrix spikes, blanks, surrogates, etc.) which satisfy acceptance criteria. Review raw data and quantitation report; check for false positives, false negatives, improper integration, incorrect calculations. Transfer results to LIMS.
Peer Scientist	Confirm calibration and QC results; check both raw data & calculations and look for system contamination. Review results on LIMS.
Department Supervisor	Help analysts resolve any problems with analysis; review and validate results.
Quality Assurance	Confirm that all analytical runs meet acceptance criteria and all previous reviews have been done.
Laboratory Director	Confirm that all necessary data review has been performed by appropriate personnel and results are as expected.

3. **Proofreading to validate spelling, grammar and punctuation**

Responsible Party	Requirement
Client Services Dept.	Sample Receiving Technician checks own work for typographical & transcription errors. Verify sample IDs, phone numbers, purchase order and project numbers. Review by CS Manager or peer.
Analyst	Review LIMS input for spelling errors, incorrect units, data transcription errors
Peer Scientist	Report any obvious errors to analyst
Department Supervisor	Correct any errors. Verify that report comments & condition codes have been used appropriately.
Laboratory Director	Confirm that all necessary data review has been performed by appropriate personnel

4. **Database review (relates to ongoing monitoring only)**

Responsible Party	Requirement
Client Services Dept.	Generally, none.
Analyst	Compare current data to historical values & consult supervisor when results vary "significantly."
Peer Scientist	None.
Department Supervisor	Consult with analyst as needed. Perform additional database review as required.
Laboratory Director	Confirm that all necessary data review has been performed by appropriate personnel. Inform QA of any discrepancies.

5. **Final review & reconciliation with other data; comparison to "expected" results**

Responsible Party	Requirement
Client Services Dept.	None
Analyst	Reconcile available complementary data such as Scan 2/MTBE/Gasoline Range Organics. Perform ion balance calculations when requested by supervisor. Inform supervisor of any unusual results.
Peer Scientist	Generally, none
Department Supervisor	Examine "Potential Problem Report" to identify unlikely laboratory results. Review existing complementary data including ion balance, measured/calculated hardness & conductivity values, total/dissolved and total/TCLP results.
Laboratory Director	Consider relevant client project objectives. Perform final review; sign report. Inform QA of exceptions and unusual occurrences.

Signature Page

To the best of my knowledge all information contained in this document is complete and accurate.

Author: David R. Alkema Date: 10/17/00
Dave Alkema

Supervisor: Michael Jaeger Date: 10/17/00
Michael Jaeger

Laboratory Director: Michael Jaeger Date: 10/17/00
Michael Jaeger

QA Approval: Pollyann Nee Date: 17-Oct-2000
Pollyann Nee